ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

MODIFICATION OF POLYSULFONES BY RING OPENING POLYMERIZATION PROCESSES

Ph.D. THESIS

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Chemsitry Department

Chemistry Programme

JUNE 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

HALKA AÇILMASI POLİMERİZASYONU PROSESİYLE POLİSÜLFONLAR'IN MODİFİKASYONU

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FOREWORD

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TABLE OF CONTENTS

Page

ABBREVIATIONS

AFM : Atomic force microscopy
B-a : Bisbenzoxazine
Bis-A : Bisphenol A
CA : Contact angle
DCDPS : 4,4′-dichlorodiphenyl sulfone
DFDPS : Difluorodiphenyl sulfone
DGEBA : Diglycidyl ether of bisphenol A
DMA : Dynamic mechanical analysis
DMAC : Dimethylacetamide
DMSO : Dimethylsulfoxide
DPn : Degree of polymerization
DSC : Differential scanning calorimetry
EtOx : 2-ethyl-2-oxazoline
FT-IR : Fourier transform infrared
G : Graft copolymer products
GPC : Gel permiation chromatography
HQ : Hydroquinone
IPN : Inter penetrating network
LCROP : Living cationic ring-opening polymerization
LCST : Lower critical solution temperature
MeOTf : Methyl trifluoromethylsulfonate
MeOTs : Methyl tosylate
MeOx : 2-Methyl-2-oxazoline
NMP : N-methylpyrrolidone
NMR : Nuclear magnetic resonance
PSU-B-a : Polysulfones with benzoxazine end groups
PSU-OH : Phenol-ended PSU telechelic
POx : Poly(2-oxazoline)
PMeOx : Poly(2-methyl-2-ozaxoline)
PEtOx : Poly(2-ethyl-2-ozaxoline)
PPrOx : Poly(2-propyl-2-ozaxoline)
PSU : Polysulfone
PES : Poly(ether sulfone)
PEK : Poly(ether ketone)
PC : Polycarbonate
PU : Polyurethane
PNIPAAm : Poly(*N*-isopropylacrylamide)
PEG : Polyethylene glycol
PrOx : 2-propyl-2-oxazoline
P*n*PrOx : Poly(2-*n*-propyl-2-oxazoline)
P*i*PrOx : Poly(2-isopropyl-2-oxazoline)
PAAm : Poly(N-alkyl acrylamide)

P-a :	*N*-Phenyl-3,4-dihydro-2*H*-1,3-benzoxazine
PP-a :	Poly(*N*-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine)
TGA :	Thermal gravimetric analysis
$\boldsymbol{T_g}$ **:**	Glass transition temperature
$\boldsymbol{T_m}$ **:**	Melting temperature
THF :	Tetrahydrofuran
UCST :	Upper critical solution temperature

LIST OF TABLES

Page

LIST OF FIGURES

Page

MODIFICATION OF POLYSULFONES BY RING OPENING POLYMERIZATION PROCESSES

SUMMARY

Polysulfones (PSU) are members of the high performance thermoplastics which possess noble features such as high strength and stiffness even at elevated temperatures, high continuous use and heat deflection temperatures, excellent resistance to hydrolysis, and acids and bases as well as good dimensional stability even in complex geometric shapes. PSUs offer further outstanding mechanical properties such as low susceptibility to environmental stress cracking and extremely high notched impact strength on the level of polycarbonate.

Despite these exceptional properties, it is necessary to modify the PSU structure to obtain several desired features. In general, polymer modification is the one of main ways to achieve such characteristics. Although it is possible to lose some original properties, the main features of the material can be maintained during the functionalization.

Modified polysulfones have been synthesized by several functionalization strategies. Functional phenolic end group is spontaneously achieved while synthesis of PSU. Thus, these telechelics can be converted to benzoxazine end-capped PSU macromonomers.

The functionalization of PSU with benzoxazine groups by means of monomer synthesis approach is described at the first part of the thesis. This approach was chosen in order to make use of the phenolic functional groups of PSU formed spontaneously. Thus, phenol-ended PSU telechelics were prepared by condensation of bisphenol-A and bis(p-chlorophenyl) sulfone in the presence of potassium carbonate. Afterwards, these telechelics were reacted with the aniline and formaldehyde to yield benzoxazine end-capped PSU macromonomers. Special emphasize was placed on thermal ring opening polymerization of the macromonomers alone or in the presence of added low molar mass benzoxazine as the concept provided the possibility of obtaining PSU networks potentially useful for membrane applications.

Polysulfones with benzoxazine end groups (PSU-B-a) were obtained using the precursor phenol-ended PSU telechelics (PSU-OH)s with different molecular weights. The structure of the polymers before and after functionalization was confirmed by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and Fourier transform infrared spectroscopy (FT-IR). Thermally activated curing behavior of these polymers was investigated by differential scanning calorimetry (DSC). Thermal and tensile properties of the crosslinked polymers obtained from PSU-B-a alone or with low molar mass benzoxazine (P-a) were studied by thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

In this part of study, a new class of thermally crosslinkable oligomers (macromonomers) consisting of polysulfone structure as backbone with benzoxazine functional groups connected to both ends has been successfully synthesized. The chemical structures of the intermediates and macromonomers were characterized by ^{1}H NMR, FT-IR and GPC. The free standing films of the reactive macromonomers can be further crosslinked by thermal activation to produce tough films with good thermal stability. The effect of the molecular weight of PSU oligomer on the curing behavior, thermal and tensile properties was investigated. The thermal and mechanical stability of the cured films could further extend the use of PSU based membranes in application under severe conditions.

Unlike to end group functionalization, aromatic rings of polysulfone backbone can be partially chloromethylated to create initiating sites for the cationic ring opening polymerization of 2-substituted 2-oxazolines. Hence, hydrophilic polyoxazoline graft arms are located on hydrophobic polysulfone backbone via "grafting from" method in which the modified PSU act as a macroinitiator. Resulting graft copolymer possesses amphiphilic character potentially useful for membrane applications.

At the second part of the work stated in this thesis, amphiphilic graft copolymers with hydrophilic poly(2-methyl-2-ozaxoline) (PMeOx), poly(2-ethyl-2-ozaxoline) (PEtOx) and poly(2-propyl-2-ozaxoline) (PPrOx) graft arms and polysulfone backbone were synthesized by means of grafting from method through cationic ring-opening polymerization in bulk with addition of sodium iodide. Chloromethylated polysulfone was used as a macroinitiator for cationic ring opening polymerization of 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline and 2-propyl-2-oxazoline monomers. Chloromethylated PSU (with 15% benzylchloride content) was synthesized by chloromethylation of UDEL Polysulfone (PSU) by means of catalysis of $SnCl_4$.

Exceptional emphesize was put on the influences of the monomer type and reaction times on the polymerization degree and the yield of the graft copolymer. The reaction times of graft copolymerization for each oxazoline monomers were varied gradually and their effect on the yield and degree of polymerization (DPn) were discussed. The structure of the polymers was confirmed^{1}H NMR and FT-IR. Glass transition temperatures of polymers were investigated by DSC. Thin films of graft copolymers were investigated by atomic force microscopy (AFM) and contact angle measurements. The observed layered morphology was consistent with the amphiphilic nature of the graft copolymers. The films showed temperature dependent surface hydrophobicity due to thermoresponsiveness of poly(2-oxazoline)s (POx)s.

In this part of study, graft copolymers with hydrophilic PMeOx PEtOx and PPrOx graft arms and PSU backbone has been successfully synthesized through the "grafting from" method. The structure, morphology and surface properties of such complexed macromolecules have been fully characterized. Controllable DPn of graft copolymers allows optimizations in the properties of graft copolymers. The graft copolymers synthesized in this work can be candidates for usage in biomaterials. Because of the amphihilic nature of copolymers, they exhibit layered morphology in thin films when the PSU volume fraction is ~0.15 and above. The temperature dependent surface hydrophobicity of PEtOx films was also observed by water CA measurements. The combination of the properties of both backbone PSU and side chain POx imply that these graft copolymers are promising biomaterials and may find many applications in various areas.

HALKA AÇIIMASI POLİMERİZASYONU PROSESİYLE POLİSÜLFONLAR'IN MODİFİKASYONU

ÖZET

Günümüzde yüksek performanslı termoplastik polimerlerin bir çok bilimsel ve teknolojik alanda kullanımı yaygınlaşmakta ve önemi giderek artmaktadır. Poli (eter sülfon) sınıfının bir üyesi olan polisülfon (PSU) yüksek sıcaklıklarda dahi koruyabildiği üstün gücü ve sertliği, yüksek sıcaklıkla işlenebilirliği ve bükülmesi, asitlere, bazlara ve hidrolize karşı çok dayanıklı olması, en kompleks şekillerde bile gösterdiği boyutsal kararlılığı ile termoplastik türleri içerisinde oldukça popüler bir konuma sahiptir.

Ancak tek başına bütün bu özellikler bazen yetmeyebilir. Uygulama alanına göre fazladan bazı özelliklerin eklenmesi gerekmektedir. Böyle durumlarda polimer modifikasyonu uygulanabilecek yöntemlerin başında gelmektedir. Modifikasyona uğramış polimer bazı özelliklerini kaybetsede önemli temel özelliklerini korumaktadır.

Modifiye edilmiş polisülfonlar farklı fonksiyonlandırma stratejeleri güdülerek sentezlenebilmektedir. Fonksiyonel fenolik uç gruplar PSU sentezi esnasında elde edilebilmektedir. Böylelikle fenol uçlu bu telekilikler (fonksiyonel oligomerler) kolaylıkla benzoksazin uç gruplu PSU makromonomerlerine dönüştürülebilir.

Tezin ilk kısmında monomer sentezi yaklaşımıyla benzoksazin uç gruplu PSU'ların fonksiyonlandırma yoluyla nasıl elde edildikleri anlatılmıştır. Bu yaklaşım benimsenme nedeni benzoksazin uç gruplu makromonomerlerin fenol uç gruplu PSU'lardan yola çıkılarak tek basamakta kolaylıkla sentezlenebiliyor olmasıdır. Fenol uç gruplu PSU telekelikleri, bisfenol-A ve bis-(p-klorofenil) sülfon'un potasyum karbonat varlığında kondansasyonu ile hazırlanmıştır. Daha sonra bu telekelikler anilin ve formaldehit ile reaksiyona sokularak benzoksazin uç gruplu PSU makromonomerleri elde edilmiştir.

Fonksiyonel fenol uç gruplu PSU'lar (PSU-OH) başlangıç monomerleri mol oranları değiştirilerek farklı molekül ağırlıklarında sentezlenmiştir. Böylelikle benzoksazin uç gruplu makromonomerler (PSU-B-a) bir önceki basamakta sentezlenen fenolik uç gruplu PSU telekeliklere bağlı olarak farklı molekül ağırlıklarında sentezlenebilmiştir. Benzoksazinin termoset özellikleri bu sayede polisülfona entegre edilmiştir. Fonksiyonlandırılmadan önceki (PSU-OH) ve sonraki (PSU-B-a) oligomerik yapıların doğrulanması ve karekterizasyonu proton nükleer magnetik resonans spectroskopisi ile (^{1}H NMR) ve Fourier transform infrared spektrofotometresiyle (FT-IR) gerçekleştirilmiştir. Bu oligomerlerin (PSU-B-a) hem tek başlarına hem de düşük molekül ağırlıklı benzoksazin monomeriyle (P-a) farklı oranlarda hazırlanmış formülasyonları termal kürleştirmeye maruz bırakılmış, diferansiyel tarama kalorimetresi (DSC) ile kürleşme kinetikleri ve termodinamik davranışları, ısıl ağırlıksal analiz (TGA) ile de termal kararlılıkları incelenmiştir.

Ayrıca bu formülasyonların uygun şartlarda kürleştirilmesiyle hazırlanan numunelerin mekanik gerilme özellikleri dinamik mekaniksel analiz (DMA) ile saptanmıştır.

Sonuç olarak polisülfon ana zinciri ve her iki uçta olmak üzere benzoksazin fonksiyonel grupları içeren ve termal yolla çapraz bağlanabilen yeni bir makromonomer türü başarıyla sentezlenmiştir. Başlangıç maddeleri ve makromonomerler ^{1}H NMR, FT-IR ve jel geçirgenlik kromatografisi (GPC) ile karakterize edilmiştir. Reaktif makromonomerler (PSU-B-a) kullanılarak film şeklinde numunler hazırlanmış, bu numuneler ısısal aktivasyonla çağraz bağlı yapıya dönüştürülerek ısısal dayanımı yüksek, sağlam ve sert filmler elde edilmiştir. PSU oligomerlerinin molekül ağırlıklarının kürleşme davranışlarını, termal ve mekanik özellikleri üzerindeki etkisi ortaya çıkarılmıştır. Kürleştirilmiş filmlerin termal ve mekaniksel kararlılıkları sayesinde bu malzemeler zor şartlarda sağlamlığını koruyabilen PSU bazlı membran uygulamalarında kullanım alanı bulabilecektir.

Tezin ikinci kısmında, amfifilik dallanmış (graft) kopolimerlerin hazırlanışı ile ilgili yaşayan katyonik halka açılımı reaksiyonunun kimyasal modifikasyonu takip ettiği yeni bir yaklaşım tarzı geliştirilmiştir. Amfifilik kopolimerin ana zincirini bir mühendislik polimeri olan PSU oluşturmuş, dallanmış yan zincirlerini ise hidrofilik özellikleriyle öne çıkan polyoksazolin (POx) meydana getirmiştir. Dallanımış POx zincirleri 2-metil-2-oksazolin (MeOx), 2-etil-2-oksazolin (EtOx) ve 2-propil-2-oksazolin (PrOx) monomerlerinin katyonik halka açılımı polimerizasyonu ile oluşturulmuştur. Polimerizasyon solvent kullanılmadan yığın içerisinde gerçekleştirilmiş, makro-başlatıcı olarak modifiye edilmiş PSU ve katalizör olarak sodyum iyodür kullanılmıştır. PSU modifikasyonu ticari bir ürün olan UDEL polisülfonun klorometilleme reaksiyonu ile fonksiyonladrırılmasıyla gerçekleştirilmiştir. Reaksiyon sonucunda elde edilen makro-başlatıcının molce %15 oranında benzil klorür içerdiği belirlenmiştir.

Tez çalışmasının bu kısmında, kullanılan monomer türünün (MeOx, EtOx ve PrOx) ve reaksiyon süresinin katyonik halka açılımı polimerizasyonu sonucunda oluşan dallanmış kopolimerin yapısal ve fizikokimyasal özellikleri üzerindeki etkileri incelenmiştir. Reaksiyon süresi her oksazolin monomeri için kademeli olarak arttırılmış ve her durum için polimerizasyon derecesi (DPn) ve veriminin nasıl etkilendiği araştırılmıştır. Makro-başlatıcı ve dallanmış kopolimer yapılarının doğrulanması ve karekterizasyonu ^{1}H NMR ve FT-IR gerçekleştirilmiştir. Polimerlerin camsı geçiş sıcaklıkları diferansiyel taramalı kalorimetre (DSC) ile incelenmiştir.. graft kopolimerlerde elde edilen ince filmler atomsal kuvvet mikroskobu (AFM) ve kontak açısı (CA) ölçümleriyle incelenmiştir. Ince filmlerin katman morfolojisinin graft kopolimerlerin amfifilik yapısıyla tutarlı olduğu gözlenmiştir. Filmlerin hidrofob özelliğinin sıcaklığa bağlı olarak değişimi poli(2-oksazolin)lerin termal duyarlılıklarından kaynaklanmaktadır.

Bu çalışmada sonuç olarak, PSU omurgası ve iyi tanımlanmış POx dallanmış zincirleri içeren amfifilik kopolimerler kimyasal modifikasyon ve katyonik halka açılımı polimerizasyonu kombinasyonu ile başarıyla sentezlenmiştir. Elde edilen kompleks makromoleküllerin yapıları, morfolojileri ve yüzey özellikleri karakterize edilmiştir. Reaksiyonun yaşayan katyonik polimerizasyon olması nedeniyle tepkime süresinin dallanmış kopolimerlerin molekül ağırlıklarına veya polimerizasyon derecesine doğru orantılı olarak etki ettiği belirlenmiştir. Polimerizasyon derecesinin kontrol edilebilir olması hedeflenen amfifilik dallanmış kopolimerin özelliklerinin

optimize edilebilmesine imkân sağlamaktadır. Hazırlanan ince filmler, PSU fraksiyonunun 0.15 ve altı olduğu durumlarda amfifilik doğalarından dolayı katmanlı morfoloji göstermektedirler. Yapılan kontak açısı ölçümleriyle poli(2-etilen-2-oksazolin) filmlerinin sıcaklığa bağlı olarak hidrofobisitesinin değişimi gözlenmiştir. PSU ana zinciri POx yan zincirlerinin özelliklerinin bileşimi sentezlenen bu amfifilik kopolimerlere başta biyo-malzeme olmak üzere daha birçok alanda kullanım alanı sağlamaktadır.

1. INTRODUCTION

Polysulfone (PSU) is a member of the high performance thermoplastics which possess noble features such as high strength and stiffness even at elevated temperatures, high continuous use and heat deflection temperatures, excellent resistance to hydrolysis, acids and bases as well as good dimensional stability even in complex geometric shapes [1]. PSU offers further outstanding mechanical properties such as low susceptibility to environmental stress cracking and extremely high-notched impact strength on the level of polycarbonate. Despite these exceptional properties, it is necessary to modify the PSU structure to obtain several desired features such as processability and film forming properties. In general, polymer modification is the one of main ways to achieve such characteristics. Although it is possible to lose some original properties, the main features of the material can be maintained during the functionalization [2]. There are two approaches to functionalize PSUs. The first one is postpolymerization modification in which the polymer is modified after polymerization. The second approach involves direct copolymerization of functionalized monomers [3-6]. Recent studies on PSU have focused mostly on combination of PSU with epoxy resins via end group functionalization or blending. Engineering thermoplastics based on PSU have been widely used to overcome the problems associated with the brittleness of epoxy-based thermosets [7-11].

Combined with the outstanding properties of PSU, it is frequently used as biomaterials since it can endure all sterilization techniques (steam, ethylene oxide, gamma radiation) [12, 13]. More recently, research on PSU have focused on membrane technologies and biomedical applications such as hemodialysis, water purification, gas separation, cell culture, drug delivery, bioartificials and fuel cells that require easy manufacturing processes allowing reproducible properties and controllable pore size [12-20]. However, the hydrophobic nature of PSU restricts its usage as biomaterials in the filtration of protein containing solutions and blood containing applications. In order to overcome problems associated with the

hydrophobicity, it is necessary to modify the PSU structure with hydrophilic groups or segments. There is a variety of modification techniques for imparting amphiphlic character to PSU. Many reports for the modification have been based on the reactive functionalization [21-24] followed by polymerization through this functional groups. Typically, sulfonation or halogenation reactions were used to introduce initiating or reactive sites for blocking and grafting of hydrophilic monomers or oligomers, respectively [25-28].

Thermally stable high performance polymers are of great interest due to their numerous applications in a variety of fields such as electronic and optical devices, biomaterials, and aerospace materials. Among them, polybenzoxazine is a relatively new phenolic system displaying a wide range of interesting features. Polybenzoxazines are formed by thermally activated ring opening polymerization of the corresponding monomers without requirement of any catalyst (Figure 1.1) [29-33]. The polymerization is usually considered to be a green process since no toxic byproducts are formed during the ring opening reaction. However, a recent study reports that some but very little amount of byproducts are formed as a side reaction depending on the substituent on the ring structure [34]. These materials exhibit near-zero shrinkage upon curing, low water absorption, high char yield, excellent electrical properties and low surface energy [35-37]. A wide range of polybenzoxazines have been obtained from monomeric or polymeric precursor which are simply prepared from a specific phenolic compound, a primary amine and formaldehyde [38-50].

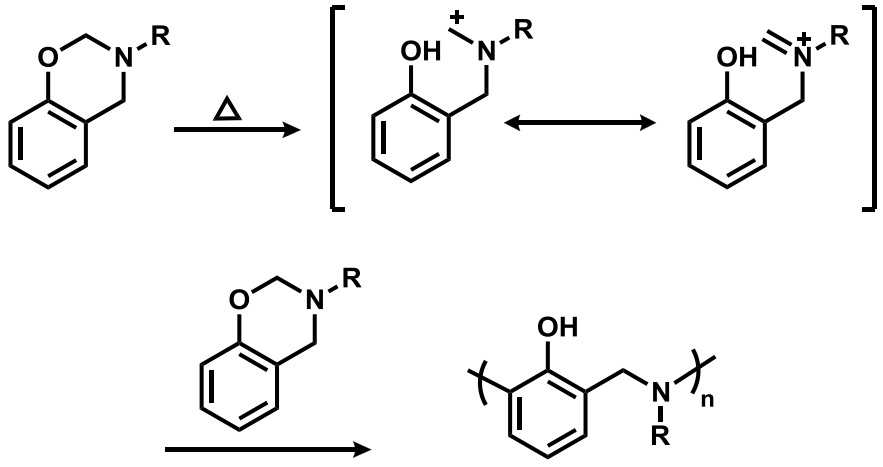


Figure 1.1 : Thermally activated ring-opening polymerization of benzoxazines.

Because of the molecular design flexibility offered by the benzoxazine synthesis, it is possible to obtain benzoxazine end-capped polymers by using suitable polymeric analogous. In most cases, polymers were functionalized by either phenolic or amine groups through several controlled/living polymerization methods using functional initiators or terminators [51-54]. Subsequent monomer synthesis in the usual manner led to the formation of flexible and processable polymers with benzoxazine units capable of forming networks upon heating. Alternative approaches include monomer synthesis from bifunctional components, step-growth polymerization of functionalized benzoxazines and the use of click chemistry [55-62]. Synthetic methodologies applied to combine benzoxazines with polymers have been treated in detail in recent review articles [63].

Polyoxazolines (POx) have aroused considerable interest in recent years and have been the subject of a number of studies concentrating on thermally activated living cationic ring-opening polymerization (LCROP) of 2-substituted derivatives with mostly ethyl, methyl, propyl or isopropyl substitutions (Figure 1.2) [64-69]. The living cationic ring-opening polymerization of 2-alkyl-2-oxazolines can be initiated by electrophilic species like alkyl halides, Lewis and protonic acids. The polymerizations proceeds without chain breaking reactions and enables to synthesize well-defined macromolecular structures including block or graft copolymers [70-74]. Poly(2-alkyl-2-oxazolines) particularly with ethyl or methyl side chains have been regarded as biocompatible material similar to the well studied poly(ethylene oxide) [75-77]. Some critical properties of the polymer like crystallinity, hydrophilicity, solubility and chirality can be designated by the nature of the alkyl substituents in the side chain. Although POx with long alkyl side chains are hydrophobic and soluble only in organic solvents, shorter side chain substituents make the polymer hydrophilic and soluble in water under a lower critical solution temperature (LCST) [78-81]. For instance, poly(2-ethyl-2-oxazoline) (PEtOx) shows a lower critical solution temperature. It is hereby considered as a thermoresponsive, non-toxic and biocompatible material [82-84].

Amphiphilic graft copolymers offer integration of distinctive properties of different polymers into one macromolecular structure.

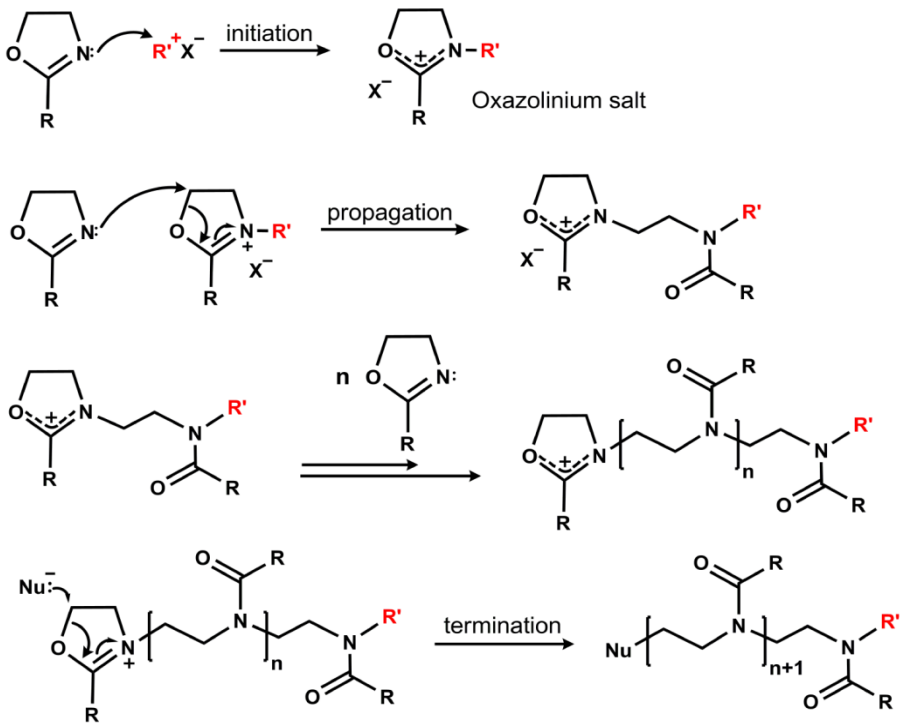


Figure 1.2 : Cationic ring-opening polymerization mechanism of 2-oxazolines.

They can be found in several self-organized formations like micelles, microemulsions and adsorbed polymer layers which make them potential candidates for biodegradable drug delivery systems and biocompatible membrane applications. Preparation of graft copolymers with hydrophilic POx graft arms and hydrophobic backbone can be carried out via grafting-from methods in which the ring opening polymerization of 2-oxazoline monomers is started by a polymeric macroinitiator [85-87].

Modified polysulfones have been synthesized by several functionalization strategies. Functional phenolic end group is spontaneously achieved while synthesis of PSU. Thus, these telechelics is then converted to benzoxazine end-capped PSU macromonomers. Special emphasize can be placed on thermal ring opening polymerization of the macromonomers alone or in the presence of added low molar mass benzoxazine as the concept provided the possibility of obtaining PSU networks.

Unlike to end group functionalization, aromatic rings of polysulfone backbone can be partially chloromethylated to function as initiating sites for the cationic ring opening polymerization of 2-substituted 2-oxazolines. Hence, hydrophilic polyoxazoline graft arms are located on hydrophobic polysulfone backbone via "grafting from" method in which the modified PSU act as a macroinitiator. Resulting

graft copolymer possesses amphiphilic character potentially useful for membrane applications.

This thesis explains the new synthetic approaches for the preparation of complex structures derived from modified polysulfones. Accordingly, thermally curable polysulfone macromonomers and cationic macroinitiators are synthesized and further used in polymerization processes to obtain novel and advantageous materials.

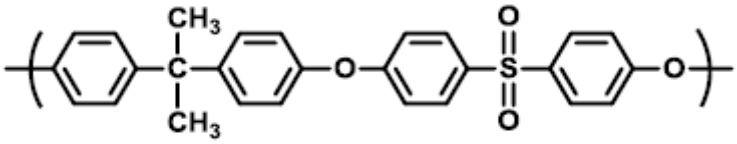
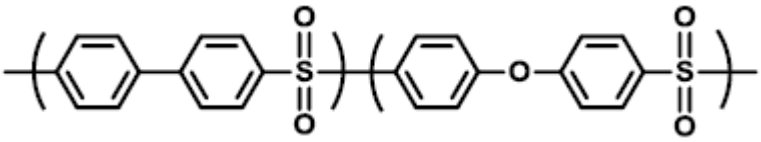
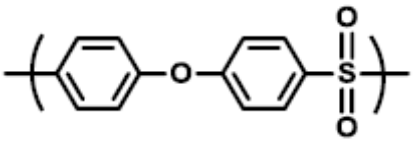
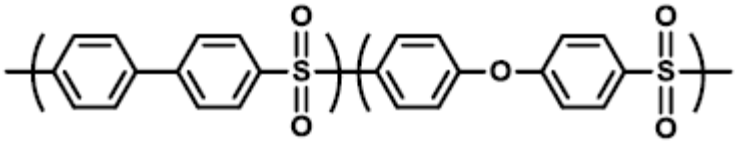
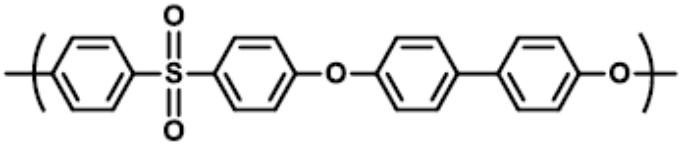
2. THEORETICAL PART

2.1 Poly(ether sulfone)s

Poly(arylene ether sulfone)s or poly(ether sulfone)s contain a class of materials used as engineering thermoplastics with excellent high temperature properties. They possess excellent properties, such as high T_g and superior thermal stability such as high strength and stiffness even at elevated temperatures, high continuous use and heat deflection temperatures, excellent resistance to hydrolysis, acids and bases as well as good dimensional stability even in complex geometric shapes [1,88,89]. Furthermore they offer outstanding mechanical properties such as low susceptibility to environmental stress cracking and extremely high-notched impact strength on the level of polycarbonate. However, there remain some undesirable features, for instance they are solvent sensitive, especially under stress, and as is typical for thermoplastics, undergo some creep when under load at high temperatures above 175°C [90,91]. These limitations prohibit their uses when solvent resistance and high-temperature dimensional stability are necessities. However, compared to poly(aryl ether ketone)s, they are considerably more liquefied at high temperatures and thus are molded and processed more effortlessly [92].

The first commercial poly(ether sulfone) was introduced in 1965 by Union Carbide (Table 2.2A). This material, now known as Udel polysulfone (PSU), has a continuous-use temperature of 150 ^{o}C and a maximum-use temperature of 170 ^{o}C, and it can be fabricated easily by injection molding in conventional machines. In 1967, Minnesota Mining and Manufacturing (3M) introduced Astrel 360, an especially high performance thermoplastic, which requires specialized equipment with extra heating and pressure capabilities for processing. ICI's polyether sulfones, introduced in 1972 Victrex and polyethersulfone (PES) 720P are intermediate in performance and processing. In the late 1970s, Union Carbide introduced Radel PSU, which has a higher level of toughness. Note that all of the commercial materials mentioned in Table 2.1 may be described as polysulfones, polyarylsulfones, polyether sulfones, or polyaryl ether sulfone [89].

Table 2.1 : Commercial poly(ether sulfone)s.

Structure	*T*g (°C)	Commercial name
	185	Udel® (Union Carbide)
	285	Astrel® (3M Corp.)
	230	Victrex® (ICI)
	250	Polyether-sulfone 720 P® (ICI)
	220	Radel® (Union Carbide)

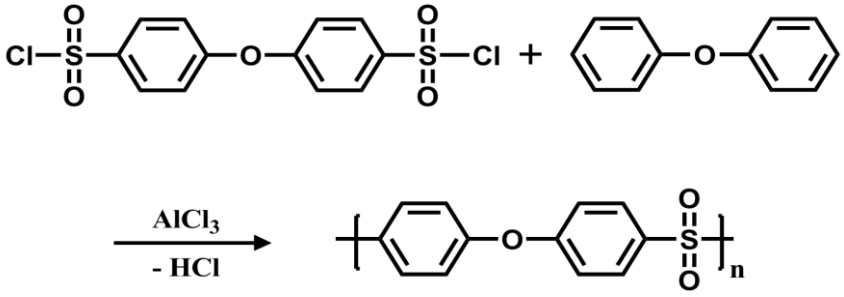
2.1.1 General pathways for the synthesis of poly(ether sulfone)s

In principle, there are two main routes to the preparation of poly(ether sulfone)s: 1- polysulfonylation (electrophilic route) and 2- polyetherification (nuclephilic route). Synthesis routes were discovered independently in three laboratories: 3M Corporation [93] and Union Carbide Corporation [94] in the United States and the plastic division of ICI [95] in the United Kingdom. Two main routes to poly(arylether sulfone)s have been reported, either a polysulfonylation process, which is a typical electrophilic aromatic substitution, or a polyether synthesis, which

is nucleophilic substitution of activated aromatic dihalides. These methods have been reviewed several times and are chemically quite different. They are opposite to each other since the polymer structures produced by single route cannot usually be produced by the other [96, 97].

2.1.1.1 Electrophilic pathway

There are two different electrophilic pathways both based on Friedal-Crafts reactions. In the first pathway poly(diphenylene ether sulfone)s were synthesiszed from the polycondensation of 4,4'-oxydibenzene-1-sulfonyl chloride with diphenyl ether (reaction 2.1) [98].



(2.1)

Poly(diphenylene ether sulfone)s are also prepared by the self-polycondensation (second pathway) of 4-phenoxybenzene-1-sulfonyl chloride [99] in nitrobenzene solution using one mole or a slight excess of $AlCl_3$ or $FeCl_3$ per gram equivalent of -SO_2Cl (reaction 2.2).

(2.2)

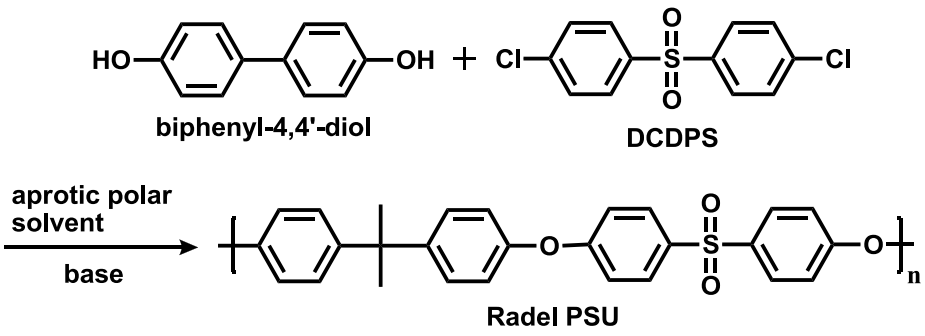
The polysulfonylation (first path) could yield polymers containing chemically linked aluminum and chlorine atoms, and in addition to the standard repeating unit different kinds of units might be made [98].

With low catalyst concentration polysulfonylations can be carried out without side reactions in contradistinction to a large extent of Fiedel-Craft catalysts. High yield polymer formation and high conversion is promotes by very reactive monomers, elevated reaction temperatures and high catalyst amounts. However, these factors also induce sulfonylation in less-favored ring positions or even multiple

sulfonylations. Therefore, structurally irregular PSUs can take place, and multiple sulfonylations on the same aromatic nucleus, in turn, can cause polymer branching and crosslinking, up to completely insoluble products. For that reason, PSUs with higher molecular weights and yields, as well as more regular structures with lower formation of insoluble products, derive from a appropriate equilibrium between the structure and reactivity of the monomers on one hand and polymerization conditions on the other. A series of bulk and solution polysulfonylation products are given in Table 2.2 [88].

2.1.1.2 Nucleophilic pathway

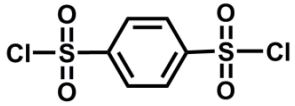
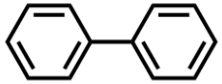
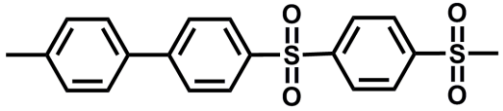
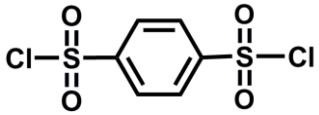
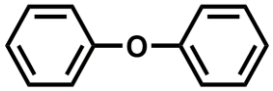
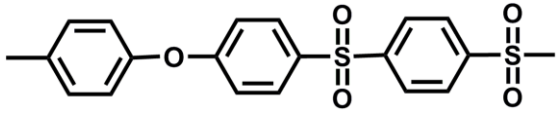
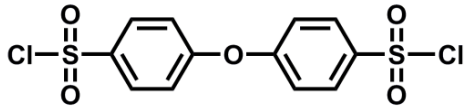
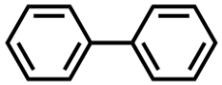
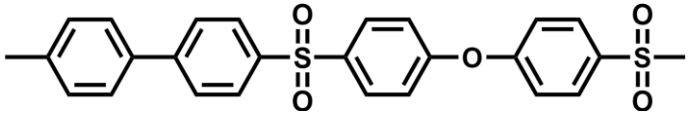
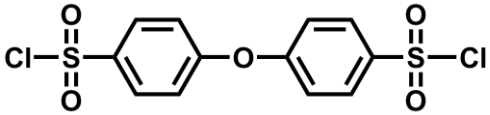
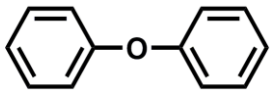
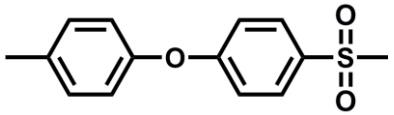
The Union Carbide Corporation introduced the first synthetic procedure based on the polycondensation of alkali metal salts of various bisphenols with activated halogeno aromatics, such as 4,4′-dichlorodiphenyl sulfone (DCDPS) (e.g, synthesis of Radel PSU is summarized in reaction 2.3) [100].



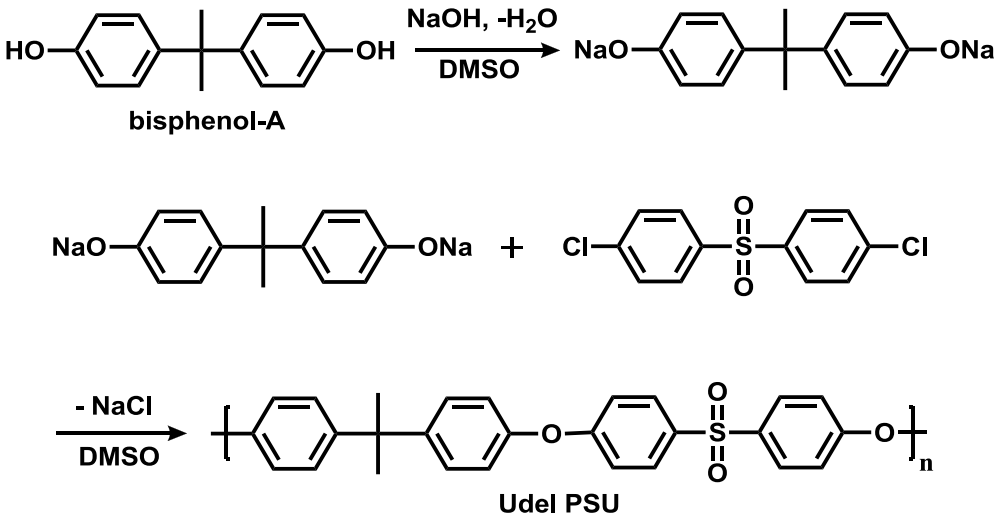
(2.3)

In nucleophilic substitution reactions, the rate of polycondensation depends on the basicity of the bisphenol salt and on the electron-withdrawing power of the activating group in the dihalide. Researches on the polyetherification mechanisms and kinetics stated that aprotic polar solvents were found to give a good reaction rate; they enhance the active concentration of the attacking base and assist the bimolecular addition step [100-103]. Several hydrolize causing side reactions could take place and hence restrain the molecular weight of the final polymeric product. A variety of combinations of base/solvent systems have been utilized for the polyetherification reactions [104–108].

Table 2.2 : Products of electrophilic polycondensation of aromatic sulfonyl chlorides and biphenyls.

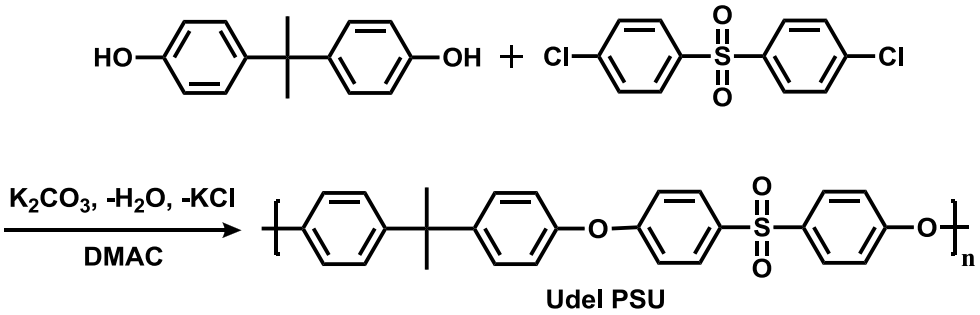
Sulfonyl chloride	Biphenyl	Repeating unit of product
		
		
		
		

Poly(arylene ether sulfone)s have been produced by either caustic/DMSO (dimethylsulfoxide)



(2.4)

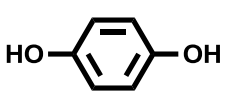
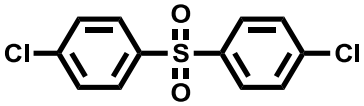
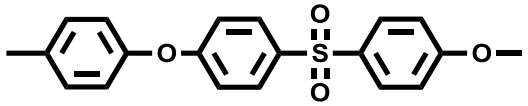
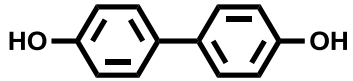
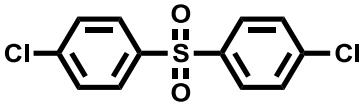
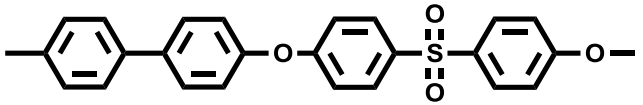
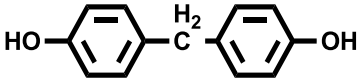
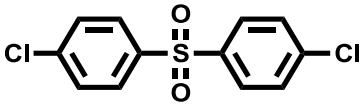
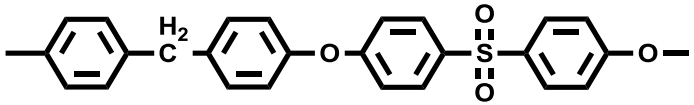
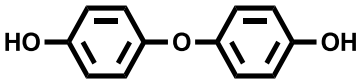
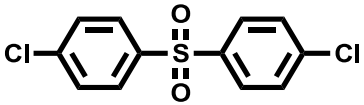
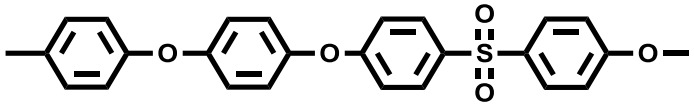
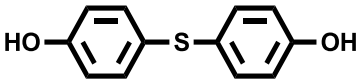
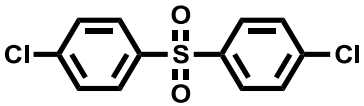
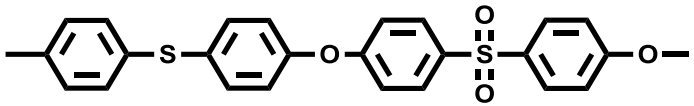
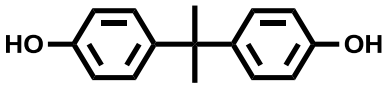
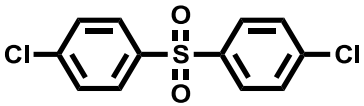
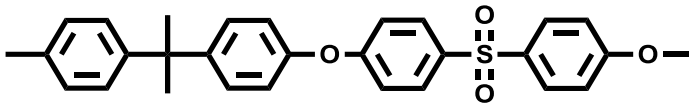
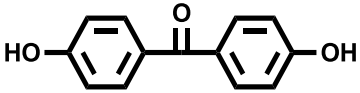
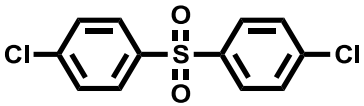
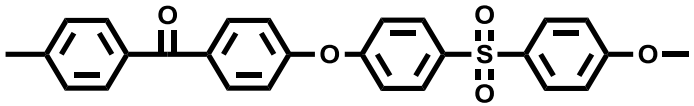
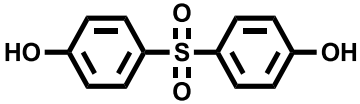
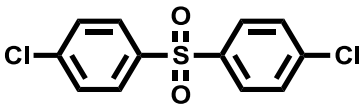
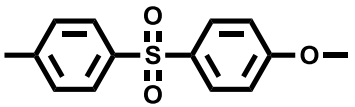
or by K_2CO_3/DMAC (N,N′-dimetyhl acetamide) techniques [106-109].



(2.5)

Even though these methods are very practical for bisphenol-A (bis-A) based systems, they are not appropriate for the synthesis of high molecular weight (MW) homopolymers or copolymers including aromatic hydroquinone (HQ) polysulfone (HQ/bisphenol PSU) because of early crystallization before reaching high molecular weight. High molecular weight polymers have been achieved by using a solvent with a high boiling point such as NMP (N-methylpyrrolidone) in the presence of K_2CO_3 [109]. By this way, hydrolytic side reactions based on nature of strong bases were also limited [106]. Temperature of reaction could be risen up to 200 °C in dimethylsulfoxide (DMSO) or sulfolane as solvents and this reaction medium was found to be necessary for successful polycondensations. Higher molecular weight and a broader application of this method seem to be achievable when diphenyl sulfone is used as the reaction medium because this sulfone is thermally more stable and allows reaction temperatures up to 300 °C [110, 111].

Table 2.3 : A variety of PSUs derived from several bisphenols and dihalide.

Bisphenols	Dihalide	Repeating unit of product	T_g (°C)
			200
			220
			180
			170
			175
			185
			205
			230

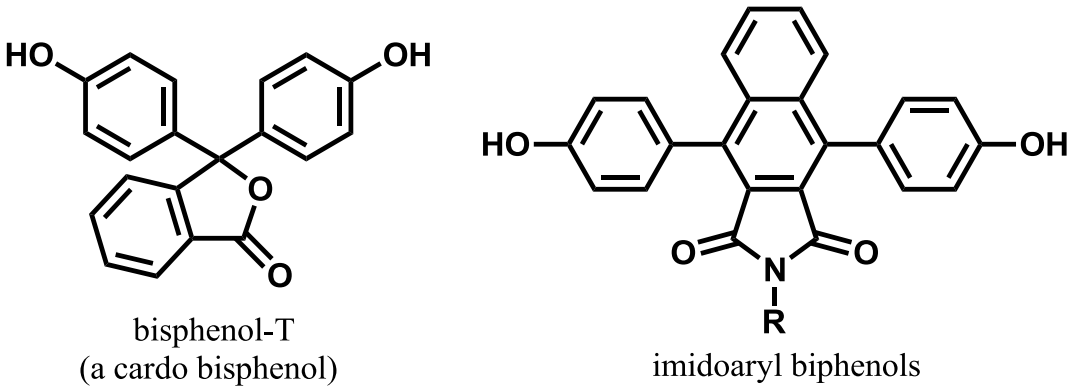
A general limitation of this procedure is that the polymeric product needs to be purified from metal salts and from the expensive solvent with high boiling point. Condensations of metal bisphenolates and a fluoroaromatic or chloroaromatic are also feasible in the absence of any solvent when reaction temperatures in the range of 280 °C – 320 °C are applied [110-112], yet the reported viscosity measurements suggest that the molecular weights obtained in this way are lower than those attainable in suitable solvents. A number of combinations of monomers (dihalides and bisphenols) and PSUs synthesized by polycondensation are given in Table 2.3 [113]

Alternatively, the bisphenols have been condensed with the activated aromatic chlorides in a two-phase solvent system via phase transfer catalyst in accordance with the principles of "interface condensation". However, the molecular weights which are achievable in a homogenous system were not obtained in this method [114, 115].

PESs were also synthesized by condensation polymerization of bis(4-fluoro phenyl) sulfone with the bistrimethylsilyl derivatives of bisphenol-A, 4,4′-dihydroxy diphenyl, 4,4′-dihydroxy diphenyl sulfone, 1,5′-dihydroxy naphthalene, 3-hydroxy benzoic acid, and 4-hydroxy benzoic acid in the presence of catalysts. Barely potassium or cesium fluoride catalysts were successful catalysts for polycondensation. At this point, the fluoride ion switches the trimethyl siloxy group into a phenolate ion, which subsequently attacks the activated fluorine-carbon bond of the difluorodiphenyl sulfone (DFDPS). The siloxy/phenolate ion equilibrium definitely tends to the left. However, the nucleophilicity of the phenolate ion is several orders of magnitude greater than that of the siloxy group, and the net effect is considerably enhanced reactivity of the bisphenol component [116].

A number of poly(imido-arylether sulfone)s have been synthesized by the nucleophilic substitution reaction of novel aromatic imidoaryl biphenols with various groups on the pendant phenyl ring with 4,4′-difluoro diphenyl sulfone [117] (Figure 2.1). The occurrence of the naphthyl imido moiety positioned between the phenyl rings of the imido aryl biphenols significantly increases the T_g and also enhances the thermooxidative stability, which may be attributed to the steric bulk and electron-withdrawing ability of the naphthyl imido group, which stabilizes the aryl ether

linkage toward oxidation, respectively. Poly(ether sulfone) with a cardo group (PES-C) using toluene, sulfolane, and anhydrous K_2CO_3 medium was reported [113]. As PES-C has a high T_g (T_g = 260°C) and is freely soluble in many common polar organic solvents, it has been considered to be useful for high-temperature-resistant ultrafiltered film materials. In a further study, PES copolymers based on phenolphthalein/4,4′-thiodiphenol with 4,4′-dichloro diphenyl sulfone were synthesisized by using a nucleophilic route involving toluene, NMP, and anhydrous K_2CO_3. It was observed that the incorporation of a small amount of bisphenol-T components into the backbone of PES-C could improve thermooxidative resistance and processing properties without deterioration of mechanical properties, but the T_g decreases [118] (Figure 2.1).



bisphenol-T
(a cardo bisphenol)

imidoaryl biphenols

Figure 2.1 : Examples of special bisphenols.

2.1.2 Properties of poly(ether sulfone)s

Regardless of their linear and regular structure, the commercial poly(ether sulfone)s are amorphous. This property might be attributed to the high degree of chain stiffness of polymer molecules that make crystallization difficult. Because of their high in-chain aromaticity and consequent high chain stiffness, the polymers have high values of T_g, which means that the processing temperatures must be above 300 ^oC [1,119].

PESs generally resist aqueous nonoxidizing acids, alkalies, salts, and aliphatic hydrocarbon solvents, such as gasoline. However, they do not resist against attack by strong acidic species such as concentrated sulfuric acid. They dissolve in chlorinated hydrocarbons (dichloromethane, chloroform, carbon tetrachloride). They swell in aromatic hydrocarbon solvents (benzene), esters (ethyl acetate), and ketones (acetone). Being highly polar, the polymer is not dissolved by aliphatic hydrocarbons

but dissolves in dimethyl formamide and dimethyl acetamide. In addition to the high heat-deformation resistance, the polymers also exhibit a high degree of chemical stability. This has been ascribed to an enhanced bond strength arising from the high degree of resonance in the structure. The polymers are thus capable of absorbing a high degree of thermal and ionizing radiation without cross-linking [119-121].

The principal features of commercial polysulfones are their rigidity, transparency, self-extinguishing characteristics, exceptional resistance to creep, especially at somewhat elevated temperatures, and good high-temperature resistance.

PESs are among the higher-priced engineering thermoplastics and so are only considered when polycarbonates or other cheaper polymers are unsuitable. In brief, poly(ether sulfone)s are more heat resistant and have greater resistance to creep, whereas polycarbonates have a somewhat higher Izod and tensile impact strength besides being less expensive.

In many fields of use PESs have replaced or are replacing metals, ceramics, and thermosetting plastics, rather than other thermoplastics. Since commercial poly(ether sulfone)s can be injection molded into complex shapes, they avoid costly machining and finishing operations. Poly(ether sulfone)s can also be extruded into film and foil. The latter is of interest for flexible printed circuitry because of its high temperature performance.

PESs have found widespread use where good dimensional stability at elevated temperatures is required and fabrication is done by injection molding. Some products made from polysulfones are electrical components, connectors, coil bobbins, relays, and appliances operating at high temperatures (e.g., hair driers, fan heaters, microwave ovens, lamp housings and bases).

PESs are transparent (though often slightly yellow), have low flammability (limiting oxygen index typically 38), and burn with little smoke production [120,121].

PESs synthesized from 4,4′-bis(4-chlorophenyl sulfonyl) biphenyl with bisphenol-S reveals a high T_g due to its chain rigidity, which arises from the phenyl and diphenyl groups, and to the presence of polar sulfone groups. The high polarity of the sulfone link leads to an electron-withdrawing effect, which delocalizes the π-electrons from the aromatic rings, producing some of double-bond character in the neighboring links. Such delocalization considerably enhances the rotational barrier around the C-

S link and consequently the chain rigidity. PESs have a low-temperature relaxation at about -100°C and a T_g at about 190°C for bisphenol-A PSU (UDEL PSU). Consequently, these polymers retain their useful mechanical properties between the temperature limits of -100°C to 175°C. The low-temperature relaxation results from two separate relaxations, first one is from the rotation in the aryl ether bond and second one is from a sulfone water complex. The former appears to be a more influential factor affecting the impact strength since bond rotation is a mechanism of energy absorption [122-124].

2.1.3 Applications of poly(ether sulfone)s

Poly(ether sulfone)s can be fabricated by melt processing techniques available for thermoplastics, injection molding, extrusion and thermoforming. Table 2.2 lists examples of early application areas and end uses for PESs [120].

The growing interest in the performance potential of sulfone polymers is leading continually to new applications for this interesting group of materials. Potable water as well as sanitary and plumbing applications represents an innovative and promising field of use. Here, sulfone polymers excel with their unbeatable combination of properties: resistance to hydrolysis, resistance to chlorine and calcium deposits as well as outstanding biocompatibility and lack of toxicological concerns in contact with hot (drinking) water.

The exceptional comprehensive strength and resistance to aging under long-term hydrostatic stress make PSU in particular an interesting material alternative to brass fittings and manifolds, especially where resistance to hot water is required, for instance, in household plumbing.

Currently, sulfone polymers are profiting from the trend among developers and designers to pay more and more attention to the appearance and esthetics of applications. The medical device field provides one example of the growing importance of the aesthetic aspect from rather unexpected areas. It has been found that high clarity and bright clean colours elicit greater acceptance by both the health care professionals as well as patients in a hospital. Originally, sulfone polymers had a yellow or amber colour, an appearance that over the years lost its att ractiveness in clinics and other areas of health care. To keep up with the trends in medical device technology and other fields of application as well as the newly encountered

requirement profiles, Solvay Advanced Polymers has in recent years introduced to the market high clarity and clarified grades of the natural sulfone polymers. High clarity polysulfone was first introduced in 2004 under the designations Udel P-1700 HC and P-3700 HC. Comparable grades based on poly(ether sulfone)s followed, for instance, the grade Radel PSU A-300 CL 128. In the same vein, brightly coloured transparent Radel R PPSU grades for durable medical component applications have been introduced recently as the Radel R-5800 TR series for use in medical device applications capable of repeated sterilization.

The interior of aircraft passenger compartments represents an additional field of application for plastics where a high degree of functionality in sought together with appealing esthetics. Thanks to its outstanding flame retardance in conjunction with minimal smoke generation and a wide range of colours that allows it to satisfy the most varied of design requirements, PPSU has been employed here successfully for over 15 years.

It is precisely this design flexibility and the opportunity to use transparent plastics with high light transmission values that has given wings to sulfone polymers in aircraft interiors. Accordingly, Solvay Advanced Polymers devel oped and introduced to the market the transparent product line Radel R-7000 TR in order to satisfy this growing demand from the aircraft industry. Applications include transparent plastic components such as room dividers and display case windows. It was the development of these new grades that opened the door for such applications.

In addition to the standard PSU grades, there are special Radel AG-340 and Radel AG-360 have been employed successfully under the hood and in headlight components, i.e. wherever low weight, dimensional stability and heat resistance are sought.

2.1.4 Limitations of polysulfones

Poly(ether sulfone)s have some of limitations. One of them is environmental stress crack resistance. Environmental stress crack resistance is not chemical degradation where a chemical reaction takes place changing the structure such as hydrolysis or ozone attack in rubbers. Actually, PESs have excellent chemical resistance in that it is not attacked by aqueous acids and bases or by oxygen and ozone. Environmental stress, cracking is a breakdown of physical structure due to a combination of applied

stress, temperature and an aggressive chemical environment [120]. In general, the aggressive environments for polysulfone are the organic ketones, esters, aromatic hydrocarbons and certain chlorinated hydrocarbons. Resistance to environmental stress cracking is difficult to predict and testing in the actual environment of use is recommended. Use of glass fiber filled polysulfones is the best solution to this deficiency.

Table 2.4 : Industrial application of poly(arylene ether) sulfones.

Application areas	End uses
Aircraft & Aerospace	Passenger service units, Luggage rack bulk heads, Astronauts' outer face mask shields
Automotive	Steering column units, Relay insulators, Pistons in load leveler
Appliances	Coffee makers, Humidifiers, Hair dryer components, Hot lather dispensers, Steam iron components, Egg cookers, Clothes steamers, Hot chocolate dispensers Water heater dip tubes, Microwave oven components,
Electrical –Electronic	Integrated circuit carriers, Connectors, Coil bobbins, Capacitor film, TV components, Brush holders, Terminal blocks, Business machine components, Printed circuit boards, Alkaline battery cases
Medical – Surgical	Respirator parts, Nebulizers, Dialysis components, Instruments, Sterilizable packages, Hospital feeding trays
Processing Equipment	Milking machine components, Ball valves, Steam table trays, Membranes for reverse osmosis, Microfiltration, Peterson separator candles

The second limitation of PESs is notch sensitivity. All polymers have some degree of notch sensitivity. The polycarbonates are outstanding in having very bad notch sensivity. The notch sensitivity of polysulfones can be overcome by proper part design that is by using generous radii or fillets to prevent stress concentration.

The weather resistance of PESs is poor. The high degree of resonance that imparts many beneficial properties also makes it a strong UV absorber. This results in poor weather resistance and makes the conventional means for improvement, UV absorbers, and defective. The best means for improving the weather resistance of polysulfone is through painting or electroplating [120].

Like all other aromatic polymers, PESs have limited resistance to photooxidation, but carbon-black-filled, stabilized PES has good weatherability. PESs have been used for many years in hot water service and at temperatures up to 141°C. PESs have poor resistance to stress cracking in hot water and in corrosive environments. The electrical properties of PES are essentially unchanged with temperature. Thus, the dielectric constant of PES is 3.37 at 20°C and increases linearly to 3.44 at 127°C. The loss tangent changes from 0.013 at 20°C to 0.017 at 127°C. In PESs, the valence angle between C-SO_2-C is 105°C and for C-O-C is 124°C. This substantial difference in the inter-ring bond angles would reduce the packing density of the unit cell. This corresponds to a substantial decrease of the melting enthalpy and of *T*m. As a result, the (T_m–T_g) interval would be quite narrow, and the crystallization would be inhibited. The value of the T_g/T_m ratio for PESs (T_g/T_m = 0.82) is substantially higher than for PEKs (poly ether ketones) (T_g/T_m = 0.66); the T_m–T_g interval of crystallizable PESs is around 100°C smaller than that of PEKs [125].

2.2 Polybenzoxazines

Various thermosetting polymers such as phenolic, melamine and epoxy resins, polyimides and vulcanized rubber are members of thermally stable high performance plastics. Phenolic and epoxy resins deserve more attention with their excellent thermal behavior, high strength level, long term mechanical and thermal stability, excellent fire resistance, smoke and toxicity characteristics, outstanding electrical and thermal insulating capabilities and low cost. By virtue of these exceptional properties, phenolic or epoxy resins have plenty of applications in various fields from commodity materials to high technology aerospace industries. However, they possess some handicaps including shrinkage and generation of volatile by-products while curing, brittleness, pure shelf life and use of catalyst for polymerization. Polybenzoxazines, the latest enhanced generation of phenolic resins, have aroused much interest in that they distinctively reveal no by-products during polymerization

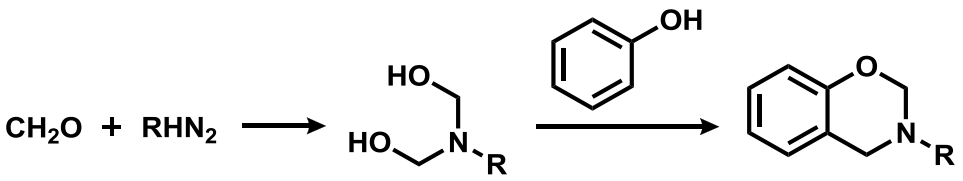
and acquire low absorption of water and also excellent dimensional stability because of a low shrinkage upon curing besides typical characteristics of traditional phenolic resins, such as heat resistance, good flame retardance, and stable dielectric constants [36,126–129]. Several kinds of polybenzoxazines have been synthesized from precursors such as benzoxazine monomers and benzoxazine incorporated or end-capped telechelics which are simply prepared from a specific phenolic compound, a primary amine and formaldehyde.

2.2.1 Synthesis of benzoxazine monomers

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution method or solventless method. Using various types of phenols and amines, having different substitution groups attached, various types of benzoxazine monomer can be synthesized. These substituting groups can provide additional polymerizable sites and also affect the curing process. In order to obtain polymeric materials, with desired properties, by tailoring the benzoxazine monomer with different functionality and a wide variety of monomers can be synthesized by using appropriate chosen phenol and amine. In this section synthesis of mono and di-functional benzoxazine monomers have been discussed.

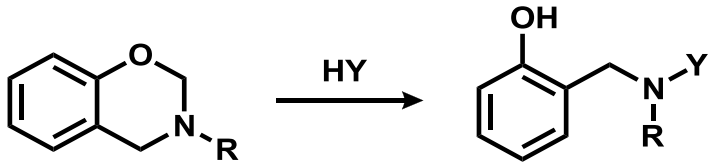
2.2.1.1 Synthesis of mono-functional benzoxazine monomers

Condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers was reported. According to the reported procedure, this reaction was performed in a solvent in two-steps. It was found that the benzoxazine ring reacts preferentially with the free *ortho* positions of a phenolic compound and forms a Mannich bridge [130]. The synthetic procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an *N*,*N*-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and *ortho* position of the phenol at the elevated temperature to form the oxazine ring [131] (reaction 2.6).



(2.6)

It has been observed that for some benzoxazines, the ring opening occurs in the presence of compounds with active hydrogen (HY), such as naphthol, indoles, carbazole, imides, and aliphatic nitro compounds even phenol (which is also one of the starting compound for synthesis) [132] and small oligomers form as by-products. Formation of the Mannich bridge structure due to the ring opening of benzoxazine in acidic medium (HY) [133] is shown below in reaction 2.7.



(2.7)

The benzoxazines derived from a strongly basic amine and a less acidic phenol found to be more stable in the hot alcohols [134]. Substituent on the benzoxazine ring affects the stability of the ring. The presence of more than one reactive *ortho* position in the initial product may lead to another aminoalkylation reaction [135]. A significantly higher yield obtained when the benzoxazine derived from phenol having an *ortho* substituent.

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, solventless synthesis in the melt state was developed [136].

The reaction mechanism and kinetics of this solventless synthesis were proposed [137]. In a typical synthesis, the reactants, *i.e.*, aldehyde, amine and phenolic precursors are physically mixed together, heated to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. In this connection, it should be pointed out that formaldehyde is not typically used as it evaporates easily and lose

stoichiometry quickly. Instead, paraformaldehyde is used. The choice for phenols and amines provides the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine polymer. The main advantages of the solventless synthetic method are improvement of reaction times compared with the traditional synthetic route and formation of fewer unwanted intermediates and byproducts.

2.2.1.2 Synthesis of di-functional and multi-functional benzoxazine monomers

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with average molecular weight around 1000 Da. Thus, no materials could be made from this approach since the thermal dissociation of the monomer competed with chain propagation reaction so that high molecular weight linear structures were unobtainable [138]. Actually, there is no convincing evidence reported for the thermal dissociation theory, though it was mentioned in the literature. Moreover, it was reported that the reduction of reactivity is due to the hydrogen bonding formation. Such phenomenon was observed in the temperature range below where reverse Mannich reaction occurs in benzoxazine chemistry [139]. To overcome this limitation, a new class of difunctional or multifunctional benzoxazine monomers [51] have been developed, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The precursor was synthesized using bisphenol-A, formaldehyde and methyl amine in different solvents and referred as B-m, (see Figure 2.2) as a reference to two of its original ingredients: bisphenol-A and methylamine. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as detected by ^{1}H NMR, FT-IR and DSC. It was observed that, the composition of the products is, to a large extent, dependent on the polarity of the solvent. This synthetic method consists of a few simple steps and can easily provide different phenolic structures with wide design flexibility.

Similar type of difunctional benzoxazine was prepared using aniline instead of methyl amine [140-141] and the pure monomer was referred as B-a and oligomers were as oligo-B-a (see Figure 2.2).

Solventless method was successfully employed for the synthesis of a series of difunctional monomers [141-142].

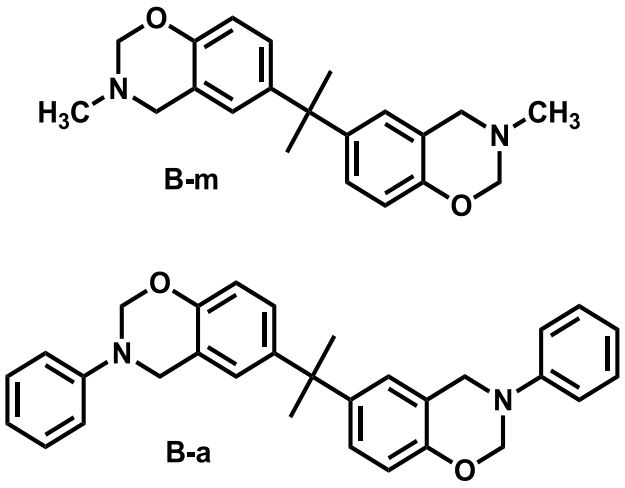
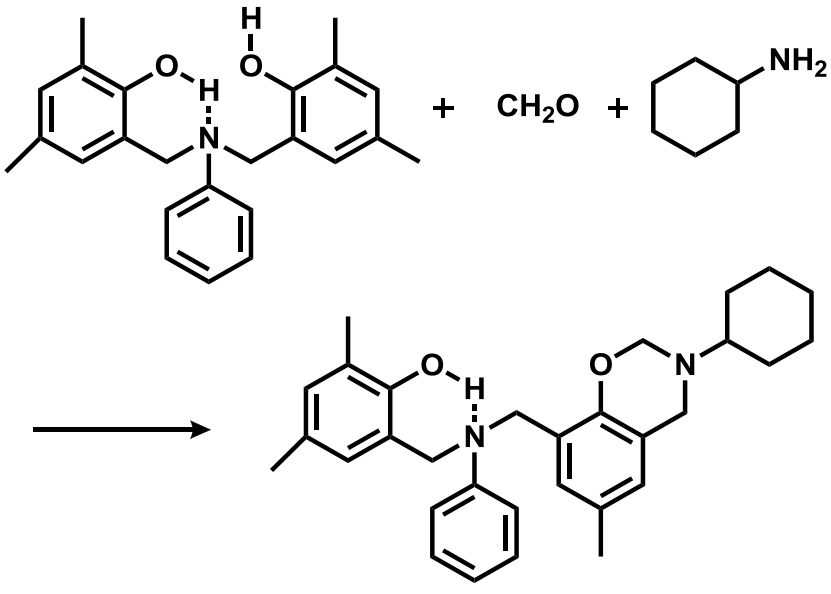


Figure 2.2: Difunctional benzoxazine monomers: B-m and B-a.

2.2.1.3 Synthesis of dimers and oligomers via step-wise controlled route

To properly understand the structures of benzoxazines and the polymers formed due to the ring opening polymerization, several model oligomers (dimers, trimers, tetramers etc.) were synthesized using a controlled step-wise route [143-146] and the synthetic strategy is shown in reaction 2.8.



(2.8)

From in-depth characterizations of these model benzoxazine oligomers by ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy a pseudo cyclic structure based on stable –OH---N intramolecular hydrogen bonding and OH---O intramolecular hydrogen bonding has been proposed and the possibility of helical structure formation in the longer chain benzoxazine oligomers has been predicted.

The stereo-structure of the reactant molecule plays an important role to control the reaction and synthesized an asymmetric product, which was not expected when considering the chemical formula of the reactants [147]. The major disadvantages of the typical polybenzoxazines are their brittleness and the high cure temperature needed to the ring opening polymerization. To address the issues related to the enhancement of the performance of polybenzoxazines is highly challenging. Two major approaches are generally considered: (1) by preparing specially designed novel monomers, or (2) by blending with a high-performance polymer or filler and fiber. Despite their usual thermal stability, the side functional groups R of the Mannich bridge, -CH2-NR-CH2-, were found to be the weakest points of the cross-linked network structures. Thermal decomposition study of the polybenzoxazines revealed that they decompose by loss of amine fragments [148]. Therefore "end-capping" to these functionalities by another polymerizable group was promising strategy to stabilize the Mannich bridge, with the expectation of further improvement of the thermal stability of the polybenzoxazines.

As per approach one, introduction of ethynyl or phenyl ethynyl [149,150], nitrile [151], propargyl [152] etc. groups, which can offer additional cross-linking site during polymerization, was found to be an acceptable choice for this purpose. According to the second approach, mechanical and thermal properties of polybenzoxazines can be improved by the preparation of copolymers, polymer alloys, composites, and polymer-clay nanocomposites.

2.2.2 Combination of polybenzoxazines with other polymeric materials

As stated previously, several approaches to overcome some of the shortcomings of polybenzoxazines, such as mechanical properties, high curing temperature and low process ability, have been proposed. These include modification of the monomer, preparation of polymer blends and composites, hybridization with inorganic materials and chemical incorporation of benzoxazine structure into polymers. The

first approach which concerns the modification of monomer in the synthesis step has been discussed in detail in the previous section. The described methods allow the possibility of preparation of a wide range of monomers with additional functionalities if not to meet completely targeted properties but at least to improve. In the following section, we will discuss the combination of polybenzoxazines with the other polymeric and inorganic materials.

Due to the relatively high toughness and the capability of intermolecular hydrogen bond formation with polybenzoxazine main chain, polycarbonate (PC) was chosen as blending material to improve the toughness of polybenzoxazines [153]. The driving force that results in the miscibility of the PC/benzoxazine blend in the entire composition range is the interaction between the hydroxyl groups of polybenzoxazine and the carbonyl groups of the PC. A solution blending method was employed for the preparation of all the blend samples. The solutions of the purified benzoxazine monomer which is based on *p*-cresol and aniline, 3-benzyl-3,4-dihydro-6-methyl-2*H*-1,3-benzoxazine (abbreviated as *p*-Ca), and PC were blended at room temperature to form a homogeneous mixture with the aid of chloroform and a transparent yellow solution was obtained. The solvent in the blended mixture was first evaporated in an ambient environment until most of the solvent was driven off, followed by removal of the residual solvent and moisture in a vacuum oven at room temperature for at least 48 h . The sample obtained above was isothermally polymerized in an air-circulated oven at 180 °C for various periods of time. It should be noted that phase separation occurs with the increase of PC content [154].

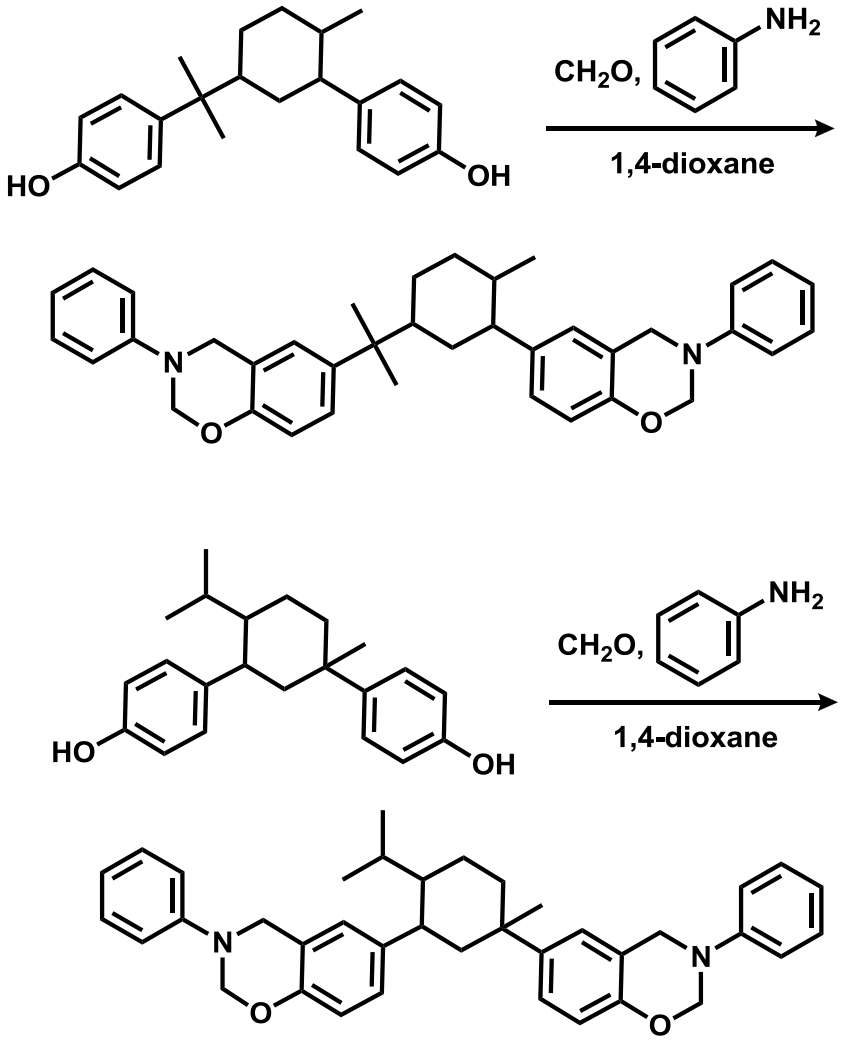
Good abrasion resistance, outstanding oil resistance, excellent low-temperature flexibility, and extraordinary processibility make polyurethane (PU) elastomers (which are the family members of segmented polymers where soft segments derived from polyols and hard segments from isocyanates and chain extenders) as one of the most attractive class of elastomers. They also exhibit the widest variety of hardness and elastic moduli that just fill in the gap between plastics and rubbers. In another words, they have the potential to tailor the materials with characteristics of either high modulus or good elasticity. However, low resistance to moisture and hydrolysis, low resistance to polar solvents, and poor thermal stability are some limitations associated with these elastomers. Generally, the acceptable thermal durability for PUs ranges from 80 °C to 90 °C, and the thermal degradation of PUs occurs at ca.

200 °C [155]. The phenolic hydroxyl groups present in the polybenzoxazine have a strong capability for reacting with PUs or their prepolymers with terminal reactive –NCO groups, which draws the motivation to prepare PU/ polybenzoxazine blends [156, 157]. Poly(urethane-benzoxazine) films were prepared by solution blending method where the PU prepolymer was mixed with various amount of a benzoxazine monomer, B-a, in THF and followed by casting on glass plates and curing by thermal treatment [158].

Inter Penetrating Networks (IPN) of PU/ PB-a was prepared by mixing B-a with PU in warm *N,N*-dimethylacetamide (DMA). The mixture was procured at 120°C for 1 h and was coated into a preheated Teflon mould at 180 °C. The mould was then kept in a vacuum oven at 120 °C for 2 h and then cured at 200 °C for 2 h [159]. A melt lending technique was used for alloying polybenzoxazine with PU and epoxy [160].

The benzoxazines were first copolymerized with an epoxy resin in order to modify their performance [161]. The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. Copolymerization led to significant increase in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness. Copolymers from polybenzoxazines and epoxy resins were also designed keeping in mind that the ring opening reactions of benzoxazines produces phenolic hydroxyl groups, which can react with epoxy resins and provide additional crosslinking points into the matrix offer a network structure [162]. Samples containing 50 mol % B-a and 50% DGEBA (diglycidyl ether of bisphenol A) was prepared and cured in a mold in the oven using the curing condition of 150°C/1 h + 170°C /1 h + 190°C /2 h + 200°C/2 h + 220°C/2 h . As it is reported that terpenediphenolformaldehyde resin possesses superior heat resistance, water resistance, and mechanical properties, terpenediphenol based benzoxazine monomers were synthesized (reaction 2.9) and cured blend samples containing 50 mol% DGEBA and 50 mol% benzoxazine monomers were prepared employing the above mentioned cure conditions [163]. The molding compounds were prepared by hot roll-kneading of a mixture of 50 phr (per hot roll-kneading), 50 phr OCNE (*o*-Cresol novolac-type epoxy resin) wax and 100 phr fused silica. Test pieces of the molding compounds were prepared by compression molding at 190°C for 20 min after preheating to required moldability

for compression molding. All test pieces were postcured at the same cure conditions to complete the cure reactions, and they were used for the various measurements. Copolymers of chain extended epoxy (40 mol%) with benzoxazine (bisphenol A and aniline based) (60 mol%) were prepared using a solutiong mixing method in acetone and investigated the effects of molecular weight of the added epoxy resins [164].



(2.9)

2.2.3 Preparation of polymers with benzoxazine moieties

Blending of benzoxazines with other polymers is one of the ways to improve the mechanical properties and processibility of polybenzoxazines. Regarding chemical linking of polybenzoxazines with the other conventional polymers the macromonomer technique was followed. The benzoxazine groups are introduced by initiation of a selected polymerization or synthesizing benzoxazines from amino or phenol functional prepolymers. In the former case, the propagating species should be unreactive towards the benzoxazine ring and N and O hetero atoms.

Here, some examples for polymers with benzoxazine moities are illustrated in Figure 2.3. Figure 2.3 (a) is benzoxazine functional polystyrene [51]; Figure 2.3 (b) is benzoxazine functional poly(ε-caprolactone) [165] and Figure 2.3 (c) is benzoxazine functional poly(methyl methacrylate) [166].

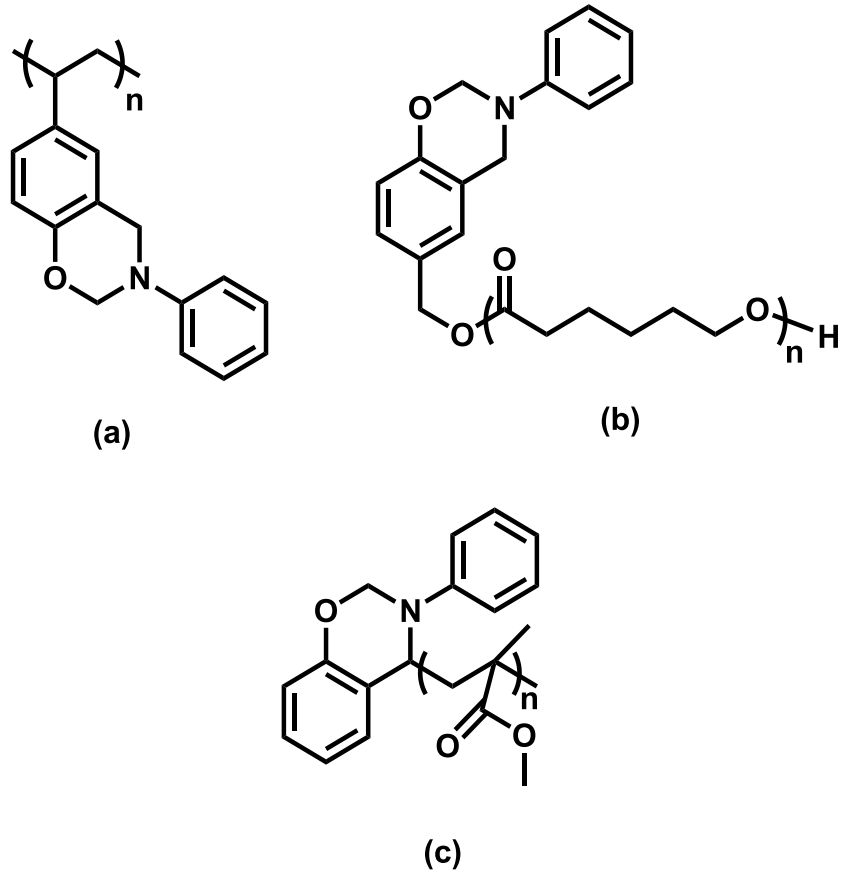
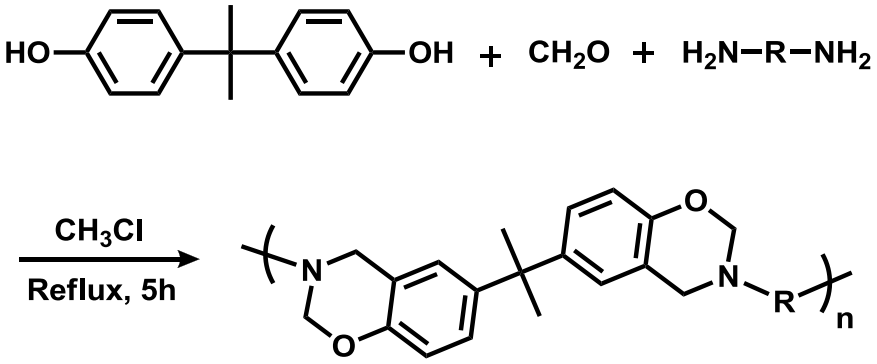


Figure 2.3 : Examples of polymers with benzoxazine moiteis.

2.2.4 Polymeric benzoxazine precursors

High molecular weight polybenzoxazine precursors can be synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde (Reaction 2.10).

The major problems associated with the preparation of such main-chain benzoxazine precursor polymers are low molecular weight and crosslinking arising from the Mannich reactions of multiple functional groups.



(2.10)

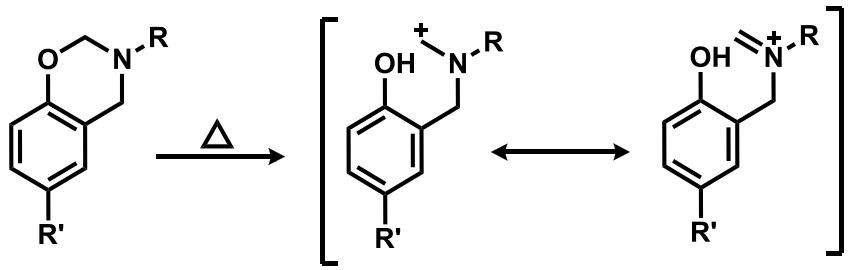
The choice of the right conditions for a Mannich reaction is critical for achieving high yields with the minimum of side reactions. In this type of Mannich polymerization, partially ring opened structures were also observed, but the ratio of the ring-closed structure in the precursor was high enough to be used as polybenzoxazine precursors. The precursor solution was cast on glass plate, giving transparent and self-standing precursor films, which was thermally cured up to 240 ^{o}C to give brown transparent polybenzoxazine films. The toughness of the cross-linked polybenzoxazine films from the high molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus, while polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass transition temperature of the polybenzoxazines derived from the high molecular weight precursors were as high as 238-260°C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability [167,168].

The only reported side-chain polymeric benzoxazine precursor is based on polyphenylene structure. Soluble and thermally curable conducting high molecular weight polybenzoxazine precursors were prepared by oxidative polymerization 3-phenyl-3,4-dihydro-2*H*-benzo[e][1,3] oxazine (P-a) alone and in the presence of thiophene (Th) with ceric ammonium nitrate in acetonitrile. The resulting polymers exhibit conductivities around 10^{-2} S cm^{-1} and undergo thermal curing at various temperatures. The partially ring-opened structure which was formed during the oxidative polymerization affects the thermal curing behavior of the polymers. The cured products exhibited high thermal stability but lower conductivity, than those of the precursors [169].

2.2.5 Reaction mechanism of ring opening polymerization of benzoxazine

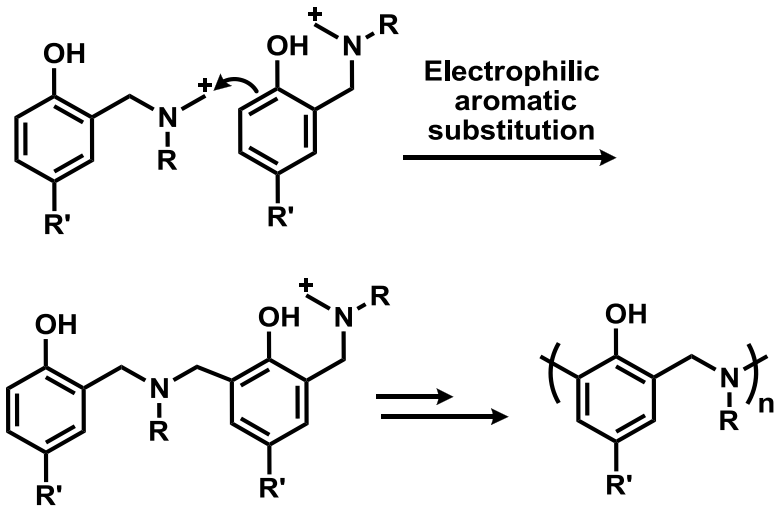
Mono-oxazine ring containing benzoxazine is a distorted structure, with the nitrogen and carbon, between oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation helps this type of six-membered ring to undergo ring-opening reaction under specific conditions. In addition, due to their high basicity (by Lewis definition) both oxygen and nitrogen of the oxazine ring can act as potential cationic polymerization initiation site and makes the ring very likely to open via a cationic mechanism [170,171].

Several mechanisms have been proposed to explain the curing of benzoxazines that the ring-opening initiation of benzoxazine results the formation of a carbocation and an iminium ion which in equilibrium (reaction 2.11) [171].



(2.11)

Polymerization proceeds via the electrophilic substitution by the carbocation to the benzene ring. This transfer occurs preferentially at the free ortho and para position of the phenol group (reaction 2.12). The stability of the iminium ion greatly affects the propagation rate because carbocation is responsible for propagation. Though, several authors have proposed different mechanism of thermal curing of benzoxazine, however, the mechanism is not well established.



(2.12)

2.2.6 Properties of polybenzoxazines

A typical polybenzoxazine, prepared from mono-functional 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a), exhibit T_g at 146 °C and 161 °C, obtained from maximum of loss modulus and the maximum of tan δ respectively of DMA results. The storage modulus decreases sharply at about 110°C. From TGA profile it was observed that, its 5 and 10% weight loss temperatures were 342 °C and 369 °C, respectively and char yield was 44% [46].

A comparative investigation on several physical properties of polybenzoxazines (PBa and PB-m), prepared by thermal curing of difunctional B-a and B-m monomers, has been reported [35]. They exhibit high T_g and significantly higher tensile moduli. than both phenolics and epoxies at the same time maintain adequate tensile strength and impact resistance.

The PB-a has a higher storage modulus in the glassy region than the PB-m, as observed from their respective room-temperature values of 2.2 and 1.8 GPa. The glass transition temperature of the PB-m (180 °C), however, is significantly higher than that of the cured PB-a material (150 °C), as determined from the maxima of the loss spectrum. As the presence of high free volumes responsible for lowering of T_g, it was postulated that the PB-a might contain a greater free volume than the PB-m.

For these polybenzoxazines the concentration of network chains is significantly lower than is typically seen in cross-linked epoxides. Though the polybenzoxazines posses low cross-linking density, they exhibit higher T_gs. The intra and intermolecular hydrogen bonding in the network of the polybenzoxazines and the

cured materials are responsible for low crosslink density [172-173]. According to many authors for epoxy resins, the crosslink density has little or no influence on stiffness or rigidity in the glassy state [174-175]. Generally, intermolecular packing, free volume, molecular architecture, and molecular weight between cross-links influence the large-strain glassy state properties, namely tensile strength and elongation at break. Higher free volume tends to enhance the mobility of network segments under load to increase ultimate elongation.

Hydrogen bonding should decrease the flexibility of a cross-linked network as it hinders rotational isomeric configurational changes and other segmental motion of chain.

When thermogravimetric analysis was employed to determine the thermal stability of these materials three major events were observed. Ishida and coworkers analyzed the evolved gases to determine the nature of these weight loss events and also proposed degradation mechanism [167]. The first event near 310 °C was due to the breakage of Mannich bridge in the phenolic Mannich bridge network which produced free aniline via a deamination reaction, along with some *N*-methyl anilines by deaminomethylation. During second event at about 400 °C, the breakup of the isopropylidene linkage of the bisphenol A occurred. The primary weight loss products were aniline and various phenolic species. Finally the last weight loss, centered near 460 °C, was attributed to the degradation of char, with release of traces of phenolic and significant amount of substituted benzene compounds [176].

2.3 Poly(2-oxazoline)s

2.3.1 2-Oxazoline

Oxazolines are five-membered heterocyclic compounds. Depending on the location of the double bond, three different oxazolines can be classified. Among them, 2-oxazoline is the most investigated and widely used compound (Figure 2.4).

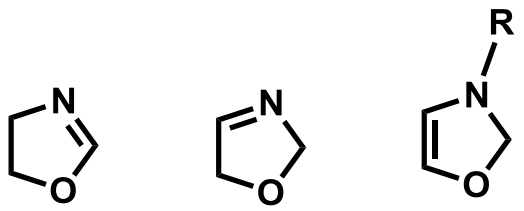


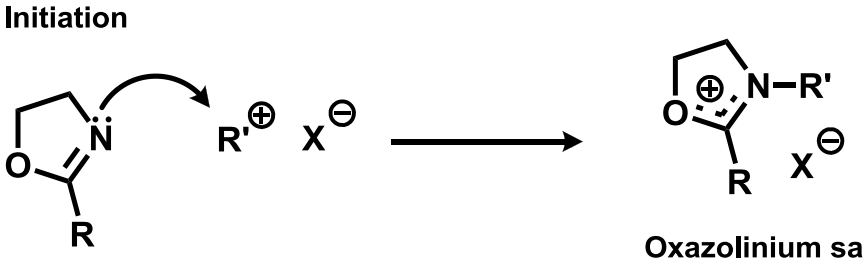
Figure 2.4 : Structures of 2-Oxazoline, 3-oxazoline and 4-oxazoline (from left to right).

2.3.2 Living cationic ring-opening polymerization (LCROP)

The 2-oxazoline can polymerize by ring-opening polymerization to form a polypeptide-analog polymer. The first research about the ring-opening polymerization of 2- oxazolines was reported in 1966 by Kagiya and co-workers [67].

It has been shown that, the ring opening polymerization reaction of 2-oxazolines was not interrupted by chain transfer and termination under proper conditions. In later reports, it was stated that in accordance with the type of initiator, the mechanism of chain growth can be cationic or covalent. When cationic initiators such as methyl triflate are used, the polymerization is cationic. The cationic propagating species of the oxazolinium salt is stable. Therefore, it was conveniently employed in the synthesis of block copolymers and end-functionalized polymers. The living cationic ring-opening polymerization (LCROP) behavior of 2-oxazolines having a diversity of 2-substituents has been comprehensively examined [74,177,178].

At the initiation step of cationic polymerization, the nucleophilic nitrogen of the 2-oxazoline ring can be converted to oxazolinium cation under the attack of electrophiles such as alkylating agents, or Lewis and Brønsted acids (reaction 2.12).

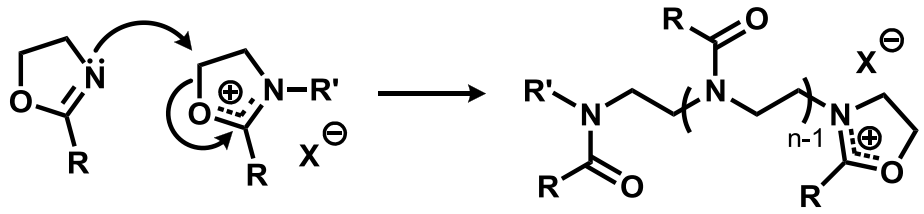


(2.13)

Throughout the propagation of cationic polymerization, the oxazolinium ring can further react with another 2-oxazoline resulting in ring opening and linear amide

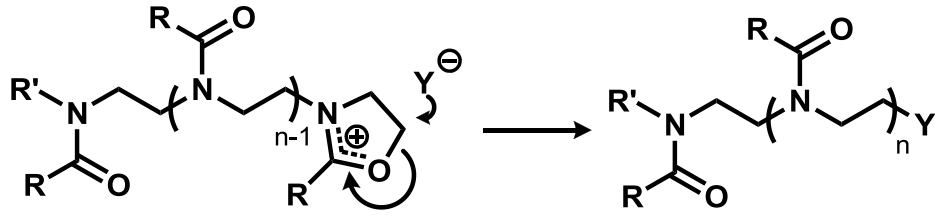
formation (reaction 2.13). This process can be repeated until a nucleophilic terminating reagent terminates the polymerization (reaction 2.14).

Propagation



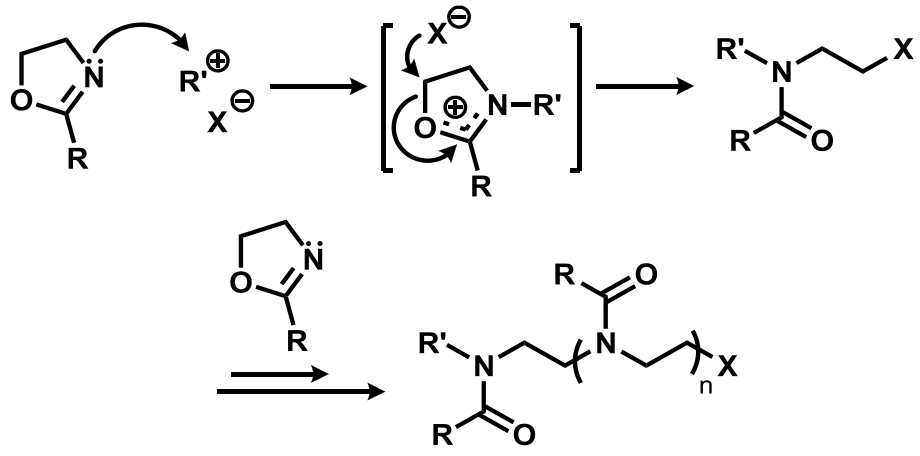
(2.14)

Termination



(2.15)

If the monomer reacts with more nucleophilic alkyl halides, e.g. methylchloride, the polymerization is slow and proceeds via a different mechanism, namely the covalent mechanism (reaction 2.15).



(2.16)

The effects of initiator types on growing species in the polymerization of several 2-oxazolines have been investigated with various initiators such as benzyl chloride, methyl iodide, methyl tosylate (MeOTs), and methyl trifluoromethylsulfonate (MeOTf) [179-182]. The consequences are shown in Table 2.5. The monomers and counteranions are positioned with respect to the order of nucleophilicities. In Figure 2.5, some of the monomers and counteranions in the polymerization of 2-oxazolines

are arranged in descending order of nucleophilicity. It is generally believed that increasing the nucleophilicity of the initiator counter ion and monomer decreases the tendency of the living cationic ring-opening polymerization (LCROP) to be ionic. With the counter ion of non-nucleophilic trifluoromethylsulfonate (OTf), the propagating species is the cation of any type of 2-oxazoline and the propagation rate increases significantly [70]. MeOTf as a commonly used initiator shows many advantages in LCROP of 2-oxazolines. Due to its high reactivity, MeOTf reacts fast with 2-oxazolines even below room temperature and the propagation starts at temperatures above 40 °C.

Fast and quantitative initiation with respect to the propagation of polymerization is crucial when preparing well-defined polymers with narrow molar mass distributions.

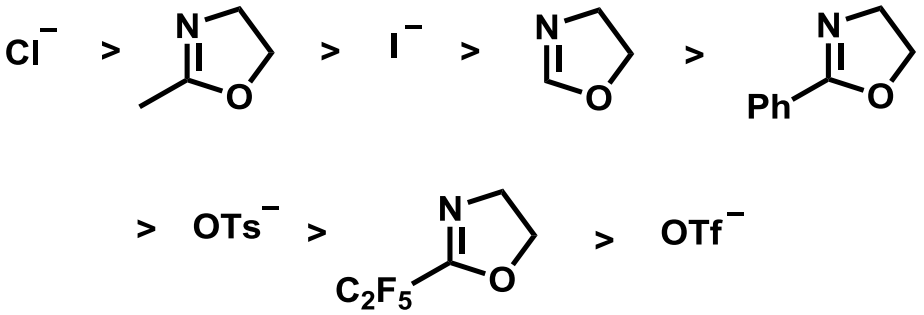
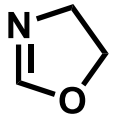
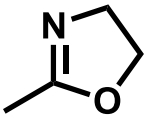
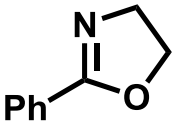
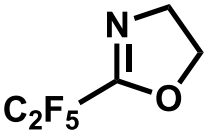


Figure 2.5 : Nucleophilicity order of monomers and counteranions.

Table 2.5 : Propagation nature of the polymerization of 2-oxazolines depending on various monomers and counterions

Monomers	Counterions			
	Cl	I	OTs	OTf
	covalent	covalent	ionic	ionic
	covalent	ionic	ionic	ionic
	-	covalent	ionic	ionic
	-	covalent	ionic	ionic

Since the initiation is nearly instantaneous and the formed oxazolinium triflate salt is sterically and electronically similar to the propagating polymer chain end, poly(2-oxazoline)s (POx) with low polydispersity indices can be prepared. Nevertheless, regardless of the living character of the cationic polymerization, side reaction can occur via chain transfer reactions particularly at elevated temperatures (T>120 °C) and at very low initial monomer and initator concentrations ($[M]_0/[I]_0$) ratios. Due to occurrence of chain transfer reactions followed by chain coupling at high monomer conversions, a shoulder in the GPC traces at high molar mass region of poly(2-ethyl-2-oxazoline)s (PEtOx) could be formed. Furthermore, yellow polymerization mixtures were achieved at low monomer concentrations, signifying the existence of side reactions. The most favorable monomer concentration between 4 mol/L and 7 mol/L was found for the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline initiated with benzyl bromide in *N*,*N*-dimethylacetamide at 100 °C [183,184].

Various synthetic opportunities have been achieved depending on the living character of the polymerization of 2-substituted 2-oxazoline, for instance modification of macromolecules with a broad variety of architectures, composition, numerous side and end functions as well as the ease of preparation of block, gradient and random copolymers. Therefore, these polypeptide-like polyamides of various architectures have established many early-stage or potential applications as stabilizers, compatibilizers and thermo-settings [185] The biocompatibility as well as stealth behavior of POx triggered the application of POx in the biomedical field [65,186-188]. Besides, water soluble POx with a lower critical solution temperature (LCST) enlarged the research area for thermo-responsive or so called “smart” materials [189].

2.3.2.1 Cationic initiators

Different kinds of cationic initiators have been used for the polymerization of 2-oxazolines [190-196]. Lewis acids, strong protic acids and their esters, and alkyl halides are typical initiators, and are listed in Table 2.6. Allyl-type dihalides, i.e. 1,4-dibromo-2-butene and 3-iodo-2-(iodomethyl)-l-propene, were utilized as bifunctional initiators. The degree of polymerization (DPn) values of the polymers agreed well with the feed ratios of the monomer to initiator. A kinetic study disclosed that the

polymerization of 2-methyl-2-oxazoline using these bifunctional initiators is a fast-initiation-slow-propagation system. As a bifunctional initiator, xylylene diiodide and dibromide are also useful (Figure 2.6) [197].

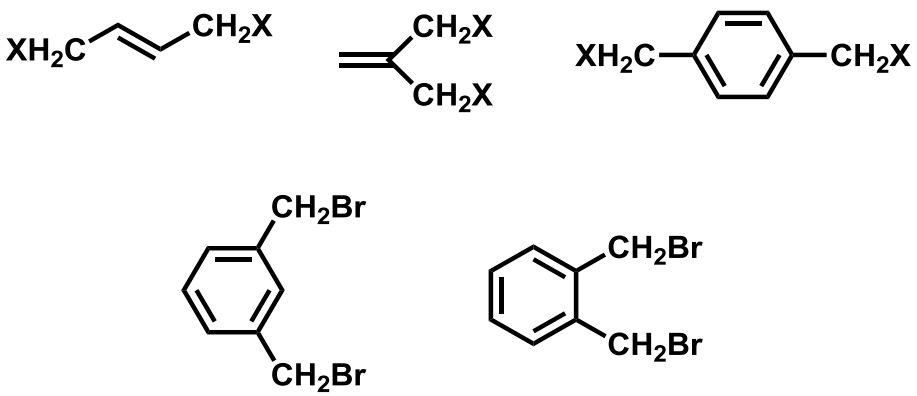
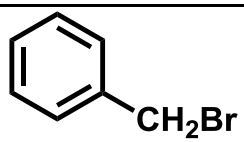
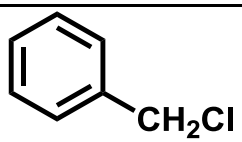
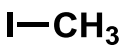
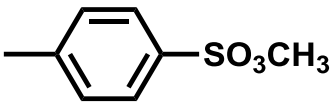
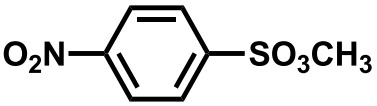


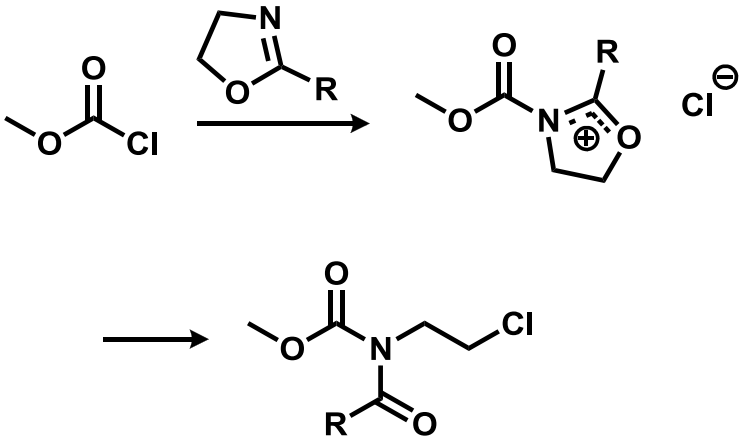
Figure 2.6 : Examples of bifunctional cationic initiotors.

Table 2.6 : Types of initiators for polymerization of 2-oxazolines

Initiator types	Examples		
Alkyl halides			
Protonic acids	CF_3SO_3H	H_2SO_4	HBr
Lewis acids	BF_3	SbF_5	$AlCl_3$
Sulfonate esters			

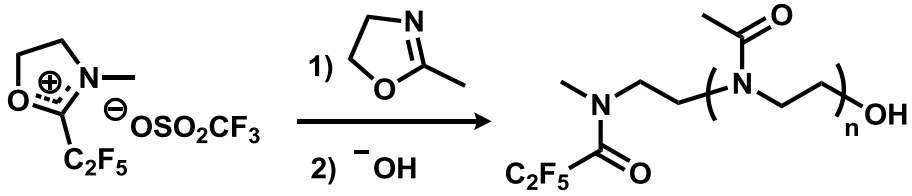
It has been shown that, a strong acylating reagent alkyl chloroformates initiate the polymerization of 2-oxazolines. The benefit of this initiator system is that chloroformates of a variety of alcohols are effortlessly obtainable by the reaction with phosgene or more expediently with diphosgene and trichloromethyl chloroformate. Methyl chloroformate reacts with 2-oxazolines with acylation and ring-opening (reaction 2.17). Upon addition of potassium iodide or silver triflate as co-initiator, propagation of 2-oxazolines proceeded efficiently [191]. Trifunctional tris(chloroformate) initiator could be prepared by the reaction of 2,2-

bis(hydroxymethyl)-1-butanol and diphosgene. This initiator was used to synthesize a three-armed star polymer [191].



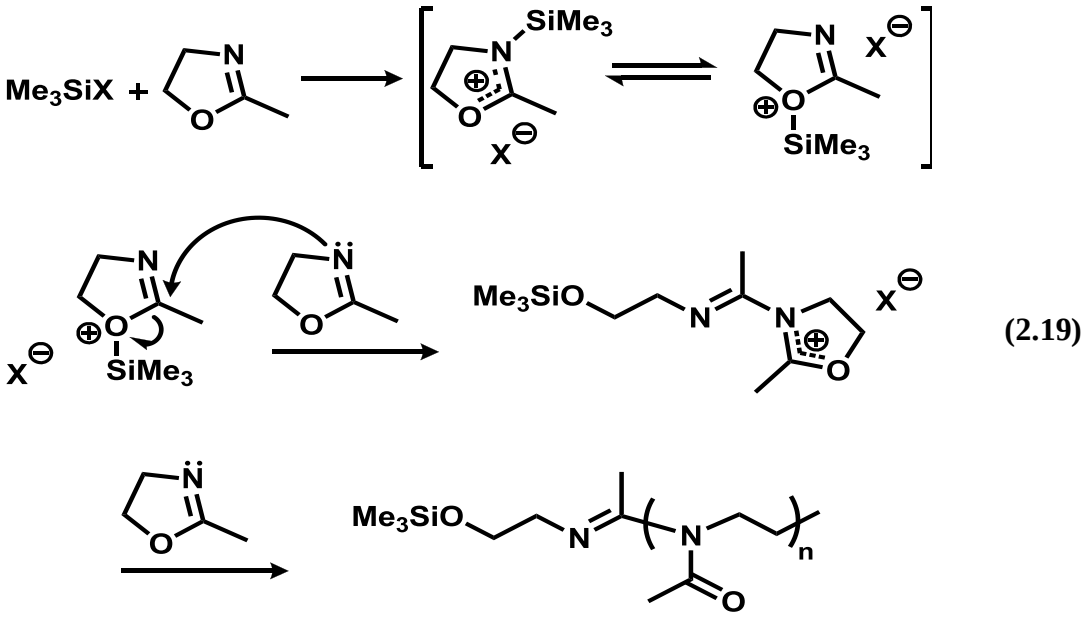
(2.17)

Oxazolinium salts such as 2-(perfluoroalkyl)-2-oxazolines and MeOTf have been used as initiators. Fluorine-containing nonionic surfactants were prepared by the polymerization of 2-methyl-2-oxazoline with the initiator of 1:1 adducts (reaction 2.18). Although these perfluoroalkyl-substituted 2-oxazolines are polymerizable monomers, a single unit is introduced precisely at the initiating end by the onium salt initiator method [198].



(2.18)

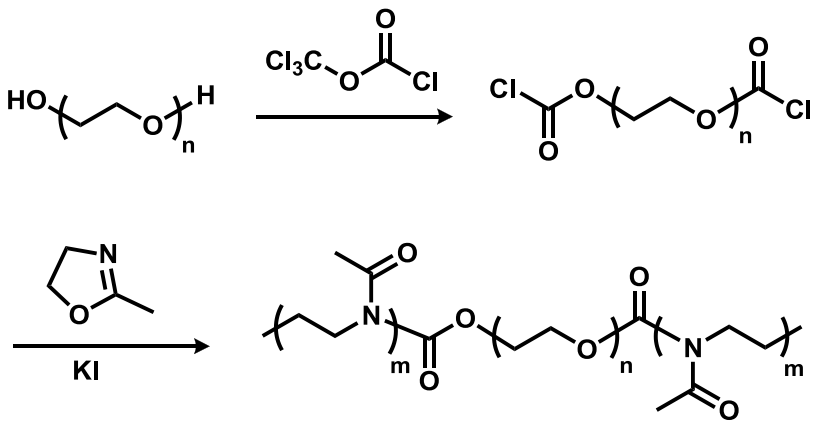
Tetracyanoethylene, 7,7,8,8-tetracyanoquinodimethane, and 2,4,7-trinitrofluorenone as organic electron-acceptors were used as initiators for the polymerization of 2-methyl-2-oxazoline, regarded as a donor. Initiation carries on by charge transfer complexes formed between the monomer and the acceptor [196]. An extraordinary mode of initiation was observed in the polymerization of 2-methyl-2-oxazoline with trimethylsilyl trifluoromethanesulfonate and trimethylsilyl iodide. The formation of the N-(trimethylsilyl)-2-methyl-2-oxazolinium cation is reversible because of a fast exchange process. The trimethylsilyl initiator is finally attacked by the oxygen atom of the monomer, generating the O-(trimethylsilyl)-2-methyl-2-oxazolinium cation. Another monomer molecule reacts at the 2-position of the onium salt, leading to an unusual ring-opening. The resulting imine dimeric cation gradually reacts with excess monomer through normal propagation (reaction 2.19) [199].



(2.19)

2.3.3 Synthesis of polyoxazoline based block or graft copolymers

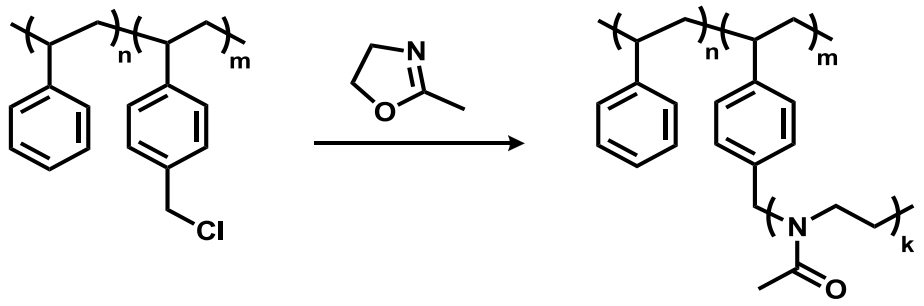
A number of graft and block copolymers having polyoxazoline chains have been reported [87,200-207]. 2-Oxazolines are useful compounds for the architectural control of polymeric materials. Various applications of oxazoline polymers are based on the structures of block and graft copolymers. The reaction with phosgene or trichloromethyl chloroformate, poly(ethylene glycol) was found to form a bifunctional macroinitiator. Polymerization of 2-methyl-2-oxazoline with this macroinitiator in the presence of potassium iodide produced an ABA-type triblock copolymer (reaction 2.20) [200].



(2.20)

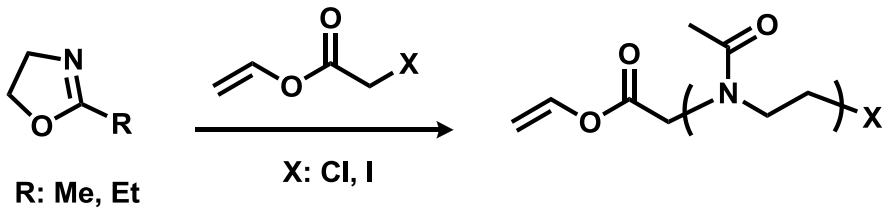
The preparation of poly[styrene-*g*-(N-acetylethylenimine)] was achieved by the macromonomer methodand by the polymerization of 2-methyl-2-oxazoline with a

chloromethylated polystyrene initiator or with an amine-containing polystyrene terminator (reaction 2.21). It is been well known that macromonomers provide a versatile method to synthesize graft copolymers having well-defined structures [87,201-203].



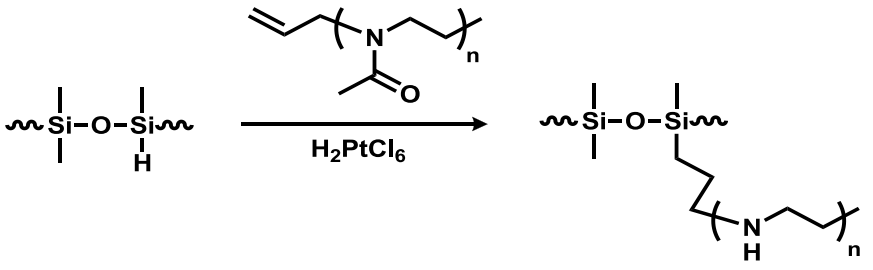
(2.21)

The macromonomers were also obtained by the reaction of acryloyl or methacryloyl chloride with an ω-hydroxy-polyoxazoline given by the hydrolysis of the propagating species of the living polyoxazoline under basic conditions. Copolymerization of these macromonomers with methyl methacrylate, styrene, or acrylamide was examined. Polyoxazoline macromonomers having a vinyl ester group were prepared by the polymerization of 2-methyl- or 2-ethyl-2-oxazoline with the vinyl haloacetate initiator [reaction 2.22] [204]. By terminating the living polymer of 2-methyl- or 2-ethyl-2-oxazoline with diethanolamine, glycol-type macromonomers were derived [205].



(2.22)

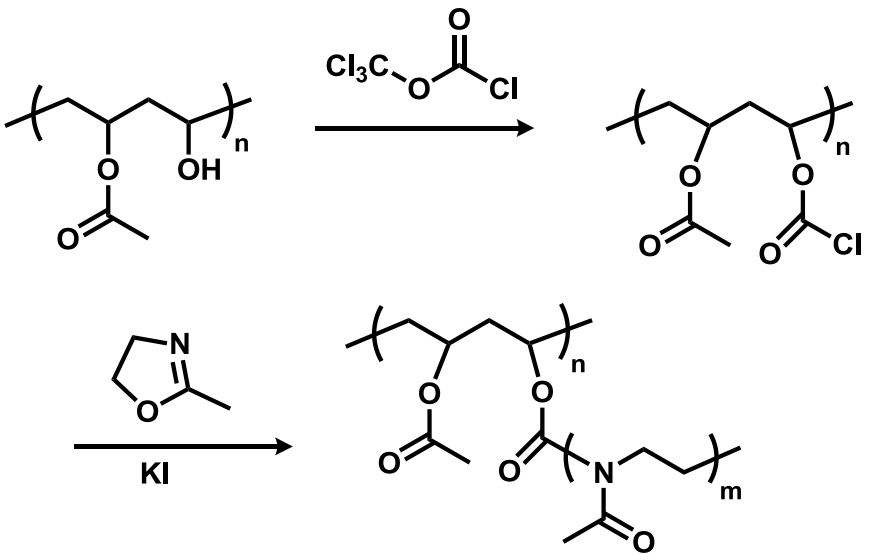
A hydrosilylation reaction was applied to synthesize a polysiloxane with a poly(Nacetylethylenimine) branches (reaction 2.23) [206].



(2.23)

By utilizing the chloroformate initiator system, graft copolymer synthesis was investigated. While chloroformate formation of poly(viny1 alcohol) is not achieved, reaction of partially hydrolyzed poiy(viny1 acetate) with phosgene or diphosgene proceeds smoothly.

Graft copolymers of poly(viny1 acetate) having poly(2-methyl-2-oxazoline) or poly(2-phenyl-2-oxazoline) side chains were obtained as shown in reaction 2.24 [207].



(2.24)

2.3.4 Thermo-responsive poly(2-oxazoline)s

Recent studies on temperature responsive polymers have focused mostly on hydrophilic poly(2-oxazoline)s. In comparison to the well-studied Poly(*N*-isopropylacrylamide) (PNIPAAm) and polyethylene glycol (PEG) systems, POx systems prepared by living cationic ring-opening polymerization (LCROP) of 2-oxazolines have numerous benefits such as easiness of access of a broad variety of end functionalities, architectures and composition. Moreover, the lower critical solution temperature (LCST) of hydrophilic POx can be modified over a broad temperature range by way of the composition and molar mass regulation.

The first investigation of the thermo-sensitivity of aqueous solutions of poly(2-ethyl-2-oxazoline) (PEtOx) was carried out by Kwei's group in 1988. It was indicated that the LCST alters depending on the polymer concentration, and cloud points in a range of 61 °C – 64 °C were observed for the molar mass of 500.000 g/mol to 20.000 g/mol [84]. In view of the fact that the first report of thermo-responsive POx, the

LCST of hydrogels, linear, homo- and coPOx were examined in details as a function of the side chain and/or end-group functionality in addition to the molar mass and concentration. In 1992, Uyama and Kobayashi stated that a cloud point in the range of 36 - 39 °C is revealed by poly(2-isopropyl-2-oxazoline) (P*i*PrOx), which makes it a suitable candidate for biomedical applicaitons [208]. Lately, Park and Kataoka reported that poly(2-*n*-propyl-2-oxazoline) (P*n*PrOx) also exhibited thermo-sensitivity in water, with a cloud point of 24 °C in a 1 wt% aqueous solution [209]. Furthermore, Schubert and co-workers [210] finely tuned the LCST of poly(2-oxazoline)s by varying composition and molar mass. The thermal transitions of these copolymers with cloud points of ~34 °C confirmed no concentration reliance, making them superior to PNIPAAm.

In addition to homopolymers, the copolymerization of different 2-oxazoline monomers allows precise control over the LCST. Park and Katoaka reported the copolymerization of 2-isopropyl-2-oxazoline (*i*PrOx) with the hydrophilic 2-ethyl-2-oxazoline (EtOx), which led to a linear increase of the cloud point up to 67 °C as a function of the EtOx content of 75 mol % [211]. Copolymerization of *i*PrOx with the more hydrophobic *n*PrOx also resulted in a linear dependence between cloud points and the composition. Recently, Jordan and co-workers further decreased the cloud point of P*i*PrOx down to 9 °C by gradient copolymerization of *i*PrOx with hydrophobic 2-*n*-butyl-2-oxazoline (BuOx) and 2-*n*-nonyl-2-oxazoline (NonOx) [212].

Additionally, Jordan and co-workers investigated the effect of end groups with different polarity on the cloud point of P*i*PrOx [213]. It was found the LCST strongly depends on the polarity of the terminal moiety especially for low molecular weight polymer. For instance, the introduction of a hydrophobic unit e.g. *n*-nonyl decreased the cloud point to 28 °C as compared to a terminal methyl group (cloud point = 47 °C). In addition, the location of the amide groups in the POx and poly(N-alkyl acrylamide)s (PAAm) resulted in different LCSTs, for example, POx pendant group modification caused a stronger shift of LCST as compared to PAAm.

Furthermore, Schlaad's group adjusted the LCST of copolymers of *i*PrOx and 2-(3-butenyl)-2-oxazoline in a range of 5-90 °C by introducing different side chain functionalities through the "click" reaction [214]. Kim and co-workers investigated thermo-responsive micellar gels formed by diblock PEtOx-b-Poly(ε-caprolactone) at

low temperature [215]. As temperature increases, gel-sol transition and subsequent precipitation occured due to the collapse of PEtOx.

Another fascinating phenomenon of POx is that some of them prove an upper critical solution temperature (UCST), above which a mixture is miscible in all proportions. The UCST is in general reliant on pressure, degree of polymerization as well as the polydispersity in polymer mixtures. The phase separation at the UCST is in general driven by unfavorable entropy; in particular, interactions between components favor a partially demixed state. Schubert and co-workers reported that poly(2-phenyl-2oxazoline) (PPhOx) showed an UCST in ethanol [216]. With addition of water to the ethanol solution, the solubility of PPhOx increased, leading to a solubility maximum in the range 6-25 wt% of water in ethanol. This maximum solubility was due to the presence of monomeric water molecules in these solvent mixtures. These water molecules formed hydrogen bonds with the polymeric amide groups, and resulted in a compatibilizing hydration shell around the polymer.

2.3.5 Biomedical applications of poly(2-oxazoline)s

Recently it was shown that poly(2-oxazoline)s (POx) were found nontoxic/biocompatible and, similar to the well established poly(ethylene oxide) (PEO) which exhibits the “stealth” effect [69]. Furthermore, in the past, Goddard revealed poly(2-ethyl-2-oxazoline) (PEtOx) as a biocompatible polymer [83]. Later on I-labeled POx was found to be discharged from mice without significant accumulation in organs [217]. Jordan and co-workers with their current studies on the biodistribution and excretion of radiolabeled poly(2-methyl-2-oxazoline) (PMeOx) and PEtOx improved these researches [186]. No accumulation in tissue and rapid clearance from blood were obtained. Chung and co-workers [217] also studied blood compatibility of PEtOx in *in vitro*. PEtOx was attached to a polyurethane film and reduced platelet adsorption was observed.

A further interesting feature of POx is their high chemical functionality so that they can be utilized as drug and protein conjugates. Polymer-drug conjugation is a multipurpose method to increase the circulation time and improve the solubility; besides, the targeting group on the polymer can deliver the drug to expected places. As the first report of PMeOx was on peptide conjugation, several studies have been carried out to investigate POx in the polymer-drug system [218]. For instance,

Jordan's group examined the PMeOx and PEtOx conjugates with in radiolabel [184,186]. In addition, Hoogenboom and co-workers showed PEtOx as a potential choice to poly(ethylene oxide) (PEO) for protein/drug conjugates [219]. Similar results were obtained for PEtOx in regard to PEO, e.g., protein-rejecting properties, drug-release profile, and *in vitro* cytotoxicity.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 For synthesis of polysulfones with benzoxazine end groups

Paraformaldehyde (Aldrich, 95%):

It was used without further purification.

Phenol (Aldrich, 99%):

It was used without further purification.

Bisphenol-A (Merck):

It was used without further purification.

Bis(p-chlorophenyl) sulfone (Alfa Aesar, 99%):

It was used without further purification.

Aniline (Acros, 99.5%):

It was distilled before use.

Chloroform (Alfa Aesar, 99,5%):

It was utilized as received.

Potassium carbonate (Merck, >99%):

It was utilized as received.

N, N-dimethyl acetamide (Acros, 99.5%):

It was utilized as received.

Toluene (Alfa Aesar, 99.5%):

It was utilized as received.

Methanol (Merck, >99%):

It was utilized as received.

3.1.2 For synthesis of polysulfone-*g*-poly(2-alkyl-2-oxazoline)s

2-Methyl-2-oxazoline (MeOx) (Aldrich, 98%):

It was distilled twice from calcium hydride under vacuum and stored under a dry nitrogen atmosphere.

2-ethyl-2-oxazoline (EtOx) (Aldrich, 99%):

It was distilled twice from calcium hydride under vacuum and stored under a dry nitrogen atmosphere.

2-propyl-2-oxazoline (PrOx) (TCI, 98%):

It was distilled twice from calcium hydride under vacuum and stored under a dry nitrogen atmosphere.

Diethyl ether (Acros, 99.5%):

It was distilled before used.

Methanol (Merck, >99%):

It was distilled before used.

Potassium iodide (KI) (Aldrich:)

It was used as received.

Polysulfone, PSU UDEL® P-1700 (M_n:29000:

It was obtained from Solvay Advanced Polymers.

Chloroform (Alfa-Aesar, 99.5%):

It was used as purchased.

Paraformaldehyde (Aldrich, 95%):

It was used as purchased.

Tin(IV)chloride ($SnCl_4$) (Aldrich, 99.995%):

It was used as purchased.

Chlorotrimethylsilane ($(CH_3)_3SiCl$) (Merck, 99%):

It was used as purchased.

3.2 Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

^1H NMR spectra of 5-10% (w/w) solutions of the intermediates and final polymers in $CDCl_3$ with $Si(CH_3)_4$ as an internal Standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.2 Infrared spectrophotometer (FT-IR)

Fourier transform infrared spectra were recorded on a PerkineElmer FT-IR Spectrum One B spectrometer.A heatable single reflection ZnSe crystal was used for sampling. The samples were directly dispensed on the ZnSe crystal and analyses were performed at room temperature.

3.2.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry analyses were performed on a PerkineElmer Diamond DSC in the range of 30-300 ^oC with a heating rate of 10 ^oC min$^-$1 under nitrogen flow.

3.2.4 Gel permeation chromatography (GPC)

Molecular weights and polydispersities of the linear telechelics were measured by gel permeation chromatography employing an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran as the eluent at a flow rate of 0,3 ml min$^-$1 at 30 ^oC. Molecular weights were determined using polystyrene standards.

3.2.5 Thermal gravimetric analyzer (TGA)

Thermal gravimetric analysis was performed on Perkine Elmer Diamond TA/TGA under nitrogen flow. Approximately 3 mg of samples were heated at a rate of 10 ^oC min^{-1}.

3.2.6 Dynamic mechanical analyzer (DMA)

The tensile properties were measured on a Perkin-Elmer Diamond dynamic mechanical analyzer model DMS6100. The measurements could be conducted under a controlled rate of

increased strain or applied stress. Tensile measurements were run for 10 min at 0.3 N min^{-1} applied stress rate using 10 mm of the film length. The tensile properties of each sample were determined from the average of at least three tests.

3.2.7 Atomic force microscopy (AFM) measurements

Thin films of graft copolymers were spin coated on silicon substrates from 1 mg/ml solutions in THF. The morphology of the films was characterized by atomic force microscopy in tapping mode. AFM measurements were carried out at room temperature in air using NT-MDT Solver P47 instrument. NT-MDT Etalon HA_NC type silicon cantilevers were used.

3.2.8 Contact angle (CA) measurements

Contact angle (CA) measurements were performed by Dataphysics OCA-20 contact angle meter. The instrument had a video-based system with CCD camera for the observation of water drop. CA was determined by SCA20 software. The instrument was equipped with temperature control chamber with a peltier system for the software controlled temperature setting.

3.3 Preparation Methods

3.3.1 Synthesis of phenol-ended PSUs

Phenol-ended PSU telechelics were synthesized within a 250 mL 2 necked round bottom flask fitted with a condenser, nitrogen inlet, a Dean Stark trap and an overhead mechanical stirrer. bisphenol-A (5 g, 22 mmol), bis(p-chlorophenyl) sulfone (3.15 g, 11 mmol) and dried potassium carbonate (3.17 g, 23 mmol) were added to 100 mL DMAC (N,N-dimethyl acetamide) and 20 mL toluene contained flask. The reaction mixture was heated under reflux at 150 ^{o}C for 4 h to dehydrate the system. Then, the reaction was stopped after about 2 h and cooled to room temperature. The solution was filtered to remove most of the salts and poured into methanol. The precipitated powder was filtered and washed several times with water

in order to remove the salts and impurities. After that the filtered solid was washed with methanol and dried in a vacuum oven at 60 ºC for about 12 h to obtain phenol-ended PSU telechelic as white powder with 62% yield. Number average molecular weight of this nearly 2000 g mol-1 telechelic (PSU-OH-2) is calculated as 1850 g mol-1 by gel permeation chromatography based on polystyrene standards and 2150 g mol-1 by ^{1}H NMR.

IR (ATR, cm-1): 3435 (─OH), 3200e3000 (Ar), 2975 (─CH_3 asym-), 2845 (─CH_3 sym-), 1322 and 1293 (O═S═O asym-), 1240 (C─O─C), 1175 and 1151 (O═S═O sym-) and 1014 (Ar).

^{1}H NMR ($CDCl_3$, ppm): δ = 7.85 (16H, O_2S─Ar─H meta position), 7.26 (16H, $(CH_3)_2C$─Ar─H ortho position), 7.07 (4H, terminal HO─Ar─H meta position), 7.00 (16H, O_2S─Ar─H ortho position), 6.94 (16H, $(CH_3)_2C$─Ar─H meta position), 6.75 (4H, terminal HO─Ar─H ortho position), 5.82 (Ar─O─H), 1.69 (30H, $C(CH_3)_2$).

Same synthesis pathway was applied to attain heavier phenolended PSU telechelics PSU-OH-4 ($M_{n,GPC}$ = 4360 g mol^{-1}, $M_{n,NMR}$ = 4000 g mol^{-1}) and PSU-OH-6 ($M_{n,GPC}$ = 6330 g mol^{-1}, $M_{n,NMR}$ = 6080 g mol^{-1}) but molar ratio of bisphenol-A and bis(pchlorophenyl) sulfone was taken 6:5 and 10:9 respectively instead of 2:1.

3.3.2 Synthesis of benzoxazine functional PSU macromonomers (PSU-B-a)

Benzoxazine functional PSU macromonomers (PSU-B-a) were synthesized from phenol-ended PSU telechelic, aniline and paraformaldehyde with molar ratio 1:10:20 respectively. Aniline (1.6 g, 17.2 mmol) and paraformaldehyde (1.03 g, 34.4 mmol) were added to 25 mL chloroform contained 50 mL two necked round bottom flask fitted with a condenser. The mixture was stirred until paraformaldehyde was completely dissolved in chloroform and, PSU-OH-2 (3 g, 1.72 mmol) was subsequently added to the solution. The reaction mixture was stirred for 24 h at reflux temperature. After the reaction was ended, the mixture was filtered and poured into methanol in order to precipitate the benzoxazine-terminated macromonomers as white powder. The precipitated powder was filtered and washed several times with water. Finally, the residual powder was washed with methanol and dried in a vacuum oven at 60 ^{o}C for about 12 h to obtain benzoxazine terminated PSU macromonomer, PSU-B-a-2 ($M_{n,GPC}$ = 2170 g mol^{-1}, $M_{n,NMR}$ = 2230 g mol^{-1}) with 84% yield. The conversion of phenolic end groups to benzoxazine functionalitieswas determined

90% by using a simple calculation based on integration values of ^{1}H NMR signals related to methyl protons belonging to Bis-A and benzoxazine ring protons.

IR (ATR, cm^{-1}): 3200-3000 (Ar), 2968 (─CH_3 asym-), 2875 (─CH_3 sym-), 1322 and 1293 (O═S═O asym-), 1238 (C─O─C), 1175 and 1151 (O═S═O sym-) and 1014 (Ar).

^{1}H NMR ($CDCl_3$, ppm): δ = 7.76 (16H, O_2S─Ar─H meta position), 7.21 (16H, $(CH_3)_2C$─Ar─H ortho position), 6.94-6.80 (40H, Ar─H), 5.11 (4H, O─CH_2─N), 4.77 (4H, Ar─CH_2─N), 1.62 (30H, $C(CH_3)_2$).

The same procedure was applied for the synthesis of PSU-B-a-4 ($M_{n,GPC}$ = 4540 g mol^{-1}, $M_{n,NMR}$ = 4230 g mol^{-1}) and PSU-B-a-6 ($M_{n,GPC}$ = 6780 g mol^{-1}, M_n,NMR = 6440 g mol^{-1}).

3.3.3 Synthesis of 3-phenyl-3,4-dihydro-1,3-benzoxazine (P-a)

3-Phenyl-3,4-dihydro-1,3-benzoxazine (P-a) was prepared via typical solventless method [220]. The general procedure is as follows; 18.6 g (0.2 mol) aniline is added slowly to the flask containing 12.0 g (0.4 mol) *p*-formaldehyde, keeping the temperature below 10°C in ice bath. The mixture is stirred for 10 min, 18.8 g (0.2 mol) phenol is added to the mixture. Then the flask heated up to 110°C for one and half an hour. The content of the flask is dissolved in ethyl ether. The ether solution was washed several times with 1 N sodium hydroxide solution and de-ionized water, respectively. Organic layer was dried with anhydrous sodium sulfate and diethyl ether was evaporated to yield light yellow viscous liquid. Solid product was formed afterapplying vacuum at 50°C in 24 h. (Yield: 68%)

^{1}H NMR ($CDCl_3$, ppm): δ = 4.49 (s, 2H, N─CH_2─Ar), 5.37 (s, 2H, N─CH_2─O), 6.79-7.30 (m, 9H, aromatics).

3.3.4 Preparation of thermally curable PSU-B-a films

For the mechanical tests PSU-B-a films were prepared by solvent casting method. Appropriate solutions containing 1 g of benzoxazine end-capped PSU macromonomer (PSU-B-a) with two different molecular weights and 0.1 g (10 wt %) of P-a in 5 mL chloroform were allowed to cast on aluminum petri dishes for 24 h at 45 ^oC. After the solvent removal, films were exposed to thermal curing at 200 ^oC for

4 h in vacuum oven. Finally brownish, transparent PSU-polybenzoxazine crosslinked films were obtained.

3.3.5 Synthesis of macroinitiator (chloromethylated PSU)

Chloromethylated PSU was prepared by the modification of PSU according to the described procedure [221]. Under inert atmosphere, PSU (5.0 g, 11.3 mmol of repeating units) was dissolved in 150 mL of chloroform in a round-bottom flask. Subsequently paraformaldehyde (1.5 g, 50 mmol), the catalyst $SnCl_4$ (0.15 mL, 1.30 mmol), and the chloromethylation agent $(CH_3)_3SiCl$ (6.4 mL, 50 mmol) were charged into the reaction vessel. The mixture was kept at 40 ^oC for 2 days under stirring. Afterward, the product was precipitated in methanol and the separated polymer was then filtered and washed several times with methanol and lastly dried under vacuum at 50 ^oC for 24 hours. 5.1 g of the product was obtained as white powder.

FTIR (ATR, cm^{-1}): 3200–3000 (Ar), 2975 (–CH_3 asym-), 2845 (CH_3 *sym*-), 1322 and 1293 (O═S═O *asym*-), 1235 (C–O–C), 1151 and 1175 (O═S═O *sym*–), 1011 (Ar), 750 (C–Cl)

^1H NMR ($CDCl_3$, ppm): δ = 7.76 (O_2S–Ar–H meta position), 7.21 (Me_2C–Ar–H *ortho* position), 7.00 (O_2S–Ar–H *ortho* position) 6.94 (Me_2C–Ar–H *meta* position), 4.50 (CH_2–Cl), 1.65 (C–Me_2).

3.3.6 Synthesis of graft copolymers (PSU-g-poly(2-alkyl-2-oxazoline)s)

All graft copolymerization reactions were performed in bulk. For every graft copolymerization, 0.050 g of the macroinitiator, 0.05 g of potassium iodide and 2 g of 2-alkyl-2-oxazoline were placed into a round-bottom flask under inert atmosphere and stirred at 120 °C. At end of the polymerization, the reaction mixture was diluted with 3 mL of chloroform and subsequently poured in 100 mL of diethyl ether to precipitate the graft copolymer. Finally, the polymer was dried under vacuum at 50 °C for 24 hours.

PSU-g-poly(2-methyl-2-oxazoline)

FTIR (ATR, cm^{-1}): 3470 (OH), 2936 (CH), 1634 (C═O), 1416 (C–H, PolyMeOx)

^{1}H NMR ($CDCl_3$, ppm): δ = 7.83 (PSU), 7.23 (PSU), 7.01 (PSU) 6.93 (PSU), 3.3–3.7 (N–CH_2, PolyMeOx), 2.0 and 2.3 (C(O)CH_3, PolyMeOx), 1.69 (PSU)

PSU-g-poly(2-ethyl-2-oxazoline)

FTIR (ATR, cm^{-1}): 3465 (OH), 2936 (CH), 1630 (C═O), 1420 (C–H, PolyEtOxa)

^{1}H NMR ($CDCl_3$, ppm): δ = 7.83 (PSU), 7.23 (PSU), 7.01 (PSU) 6.93 (PSU), 3.3–3.7 (N–CH_2, PolyEtOxa), 2.2 and 2.6 (C(O)CH_2, PolyEtOxa), 1.69 (PSU), 1.1 (CH_3, PolyEtOxa)

PSU-g-poly(2-propyl-2-oxazoline)

FTIR (ATR, cm^{-1}): 3465 (OH), 2936 (CH), 1635 (C═O), 1410 (C–H, PolyPrOxa)

^{1}H NMR ($CDCl_3$, ppm): δ = 7.83 (PSU), 7.23 (PSU), 7.01 (PSU) 6.93 (PSU), 3.3-3.7 (N–CH_2, PolyPrOxa), 2.2 and 2.6 (C(O)CH_2, PolyPrOxa), 1.7 (PSU), 1.64 (–CH_2–, PolyPrOxa), 0.96 (CH_3, PolyPrOxa)

4. RESULTS AND DISCUSSION

4.1 Synthesis, Characterization and Thermally Activated Curing of Polysulfones with Benzoxazine End Groups

4.1.1 Synthesis of benzoxazine functional PSU macromonomers

The synthesis of benzoxazine functional PSU was achieved in two steps (Figure 4.1). In the first step, phenol-ended PSUs (PSU-OH) with different molecular weights were synthesized by condensation polymerization by varying the concentration of the reactants. The reactions took place smoothly to give desired PSUs with satisfactory yields and almost quantitative phenol functionalization (Table 4.1). As can also be seen, the molecular weights of the polymers estimated from ^{1}H NMR spectra are close to those measured by gel permeation chromatography (GPC). At the second step, phenolic end groups were converted to benzoxazine functionality by applying usual monomer synthesis using aniline and formaldehyde.

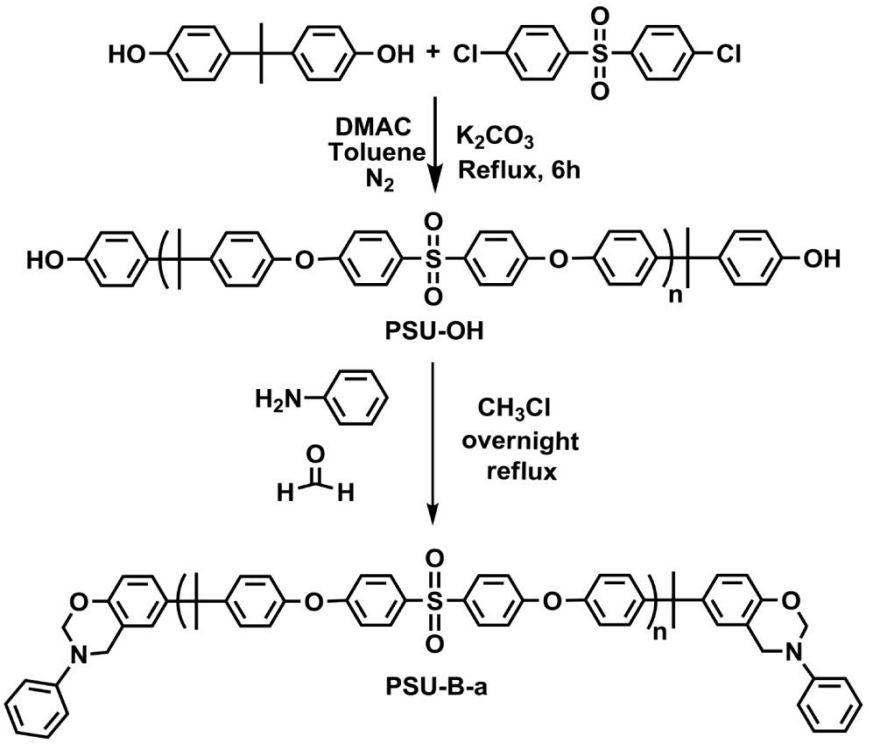


Figure 4.1 : Synthesis route of benzoxazine functional PSU macromonomers.

Table 4.1 : Synthesis[a] and molecular weight characteristics of phenol-ended polysulfone

Polymer	bisphenol-A /chlorosulfone (mol/mol)	Yield[b] (%)	$M_{n,GPC}$ [c] (g mol^{-1})	PDI	$M_{n,NMR}$ [d] (g mol^{-1})	Phenol Functionality[d]
PSU-OH-2	2/1	65	1850	1.45	2150	1.96
PSU-OH-4	6/5	71	4400	1.51	4000	1.90
PSU-OH-6	10/9	76	6330	1.65	6210	1.86

[a] Reaction Temperature: 170 ^{o}C, Time: 6h.
[b] Determined gravimetrically.
[c] Number average molecular weight of the precursor polysulfone as determined from GPC measurements based on polystyrene standards.
[d] Calculated from ^{1}H NMR spectra by comparing the intensities of signals corresponding to the outer aromatic protons adjacent to –O and inner aromatic protons adjacent to –O.

The structure of the polymers before and after functionalization was confirmed by spectral analysis. The ^{1}H NMR spectra of precursor phenolic polymer and the final macromonomer were displayed in Figure 4.2.

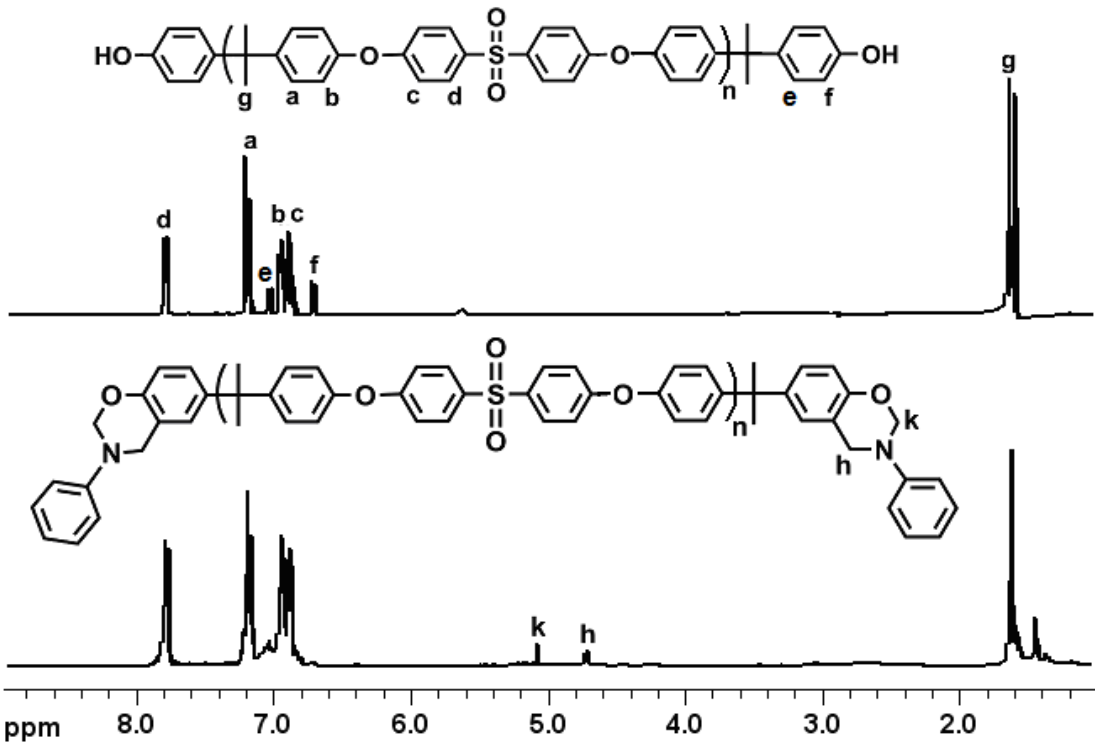


Figure 4.2 : ^{1}H NMR spectra of PSU-OH and PSU-B-a.

The signals for methyl protons of bisphenol A appear at 1.69 ppm in the both spectra. The other shifts between 6.70 and 7.86 ppm are corresponding to the aromatic protons of the poly(ether sulfone) backbone. Characteristically, aromatic protons of

terminal phenol groups appeared at 6.77 and 7.07 ppm as relatively weak signals [52]. Successful benzoxazine ring structure formation was confirmed by the disappearance of the signal at 6.77 ppm. More convincing evidence was obtained by the appearance of new peaks at around 5.11 and 4.77 ppm corresponding to methylene groups of benzoxazine ring. Notably, benzoxazine end groups overlap with the other main chain aromatic protons [222].

4.1.2 Thermally activated curing of benzoxazine functional PSU macromonomers

The obtained polymers can undergo thermally activated curing via ring opening polymerization of benzoxazine groups in a manner similar to that described for low molar mass benzoxazines in reaction 2.11 and 2.12. Schematic representation of thermally activated curing of benzoxazine functional PSU macromonomers is demonstrated in Figure 4.3.

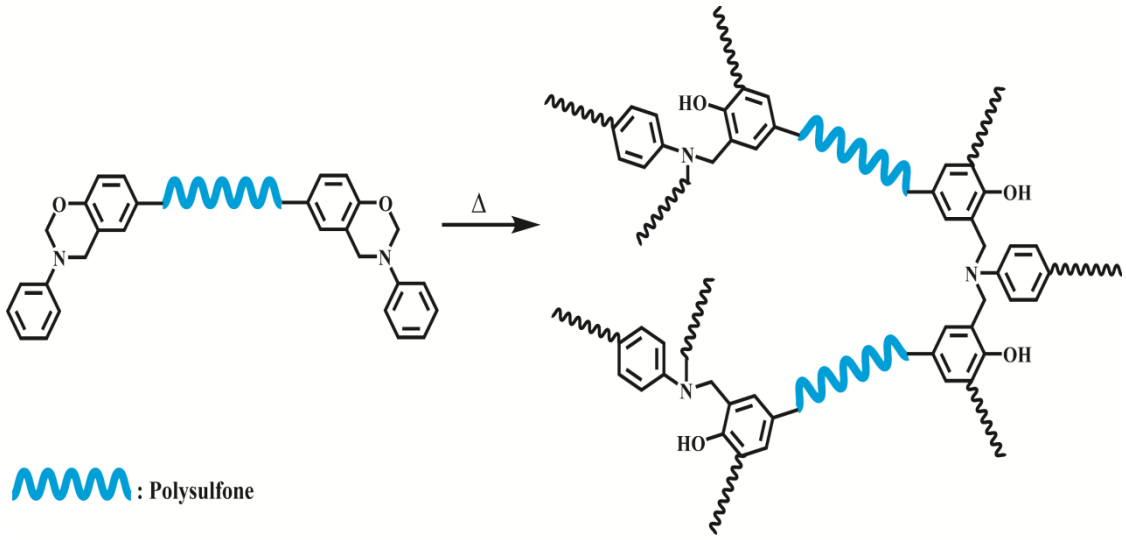


Figure 4.3 : Formation of thermally cured polysulfone/polybenzoxazine complex structure.

The effect of the molecular weight of the inner PSU segment on the thermally activated curing behavior of the macromonomers was investigated by differential scaning calorimetry (DSC). Typical DSC thermograms of PSU-B-a-2 ($M_{n,GPC}$ = 2130 g mol^{-1}) and PSU-B-a-4 ($M_{n,GPC}$ = 4540 g mol^{-1}) are presented in Figure 4.4 and Figure 4.5 respectively. The ring opening exotherm of the oxazines was observed around at 271 ^{o}C and 274 ^{o}C with onset temperatures at 256 ^{o}C and 247 ^{o}C for PSU-B-a-2 and PSU-B-a-4, respectively [223].

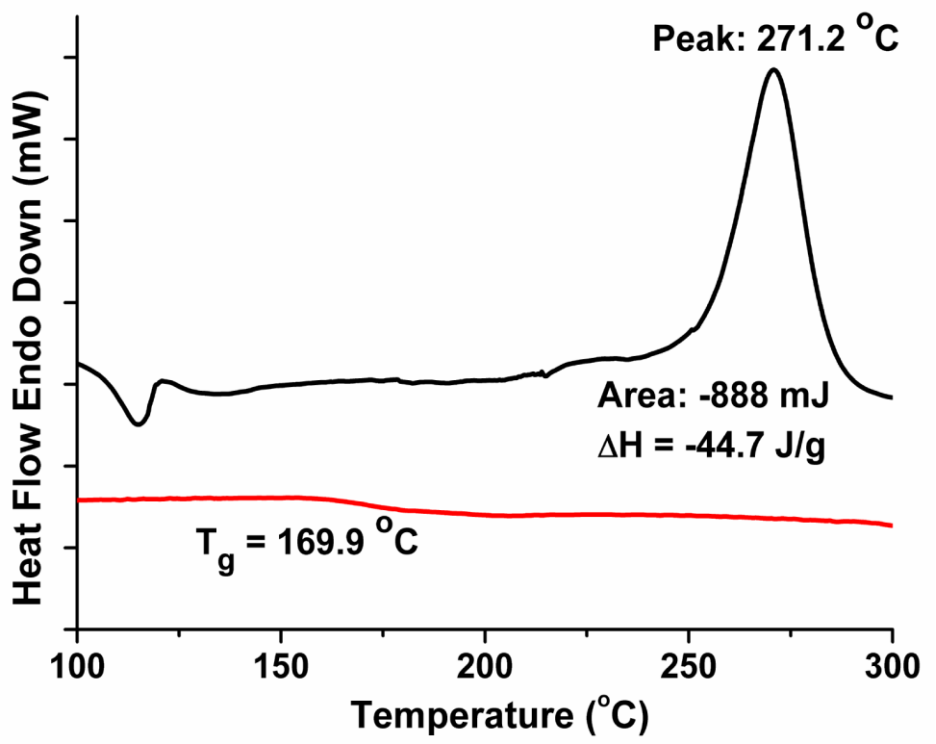


Figure 4.4 : DSC profiles of PSU-B-a-2; first run (─), second run (─).

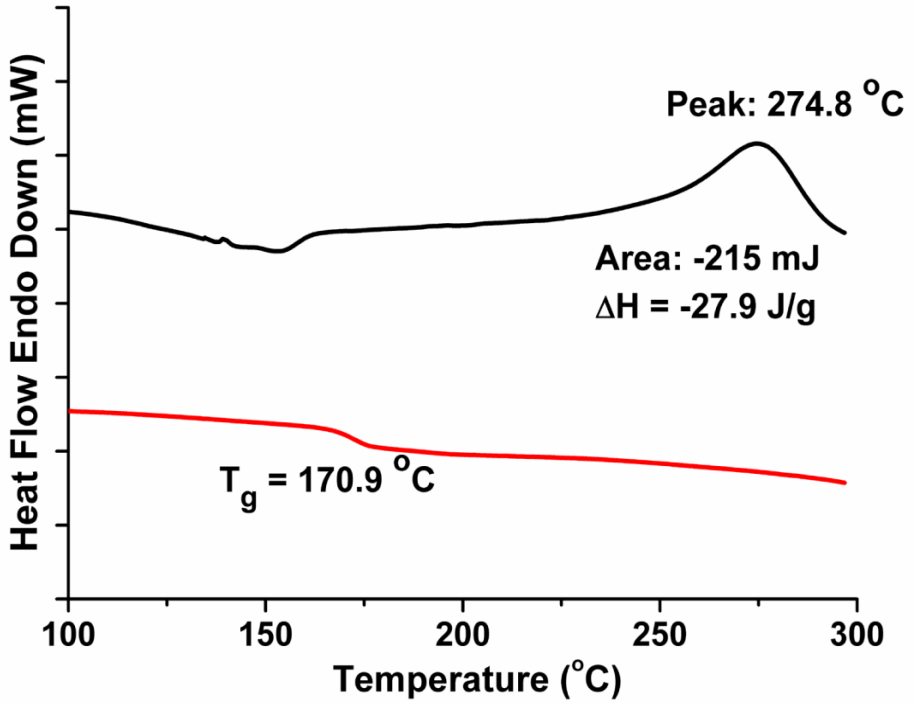


Figure 4.5 : DSC profiles of PSU-B-a-4; first run (─), second run (─).

Notably, the enthalpy change (ΔH, J.g^{-1}) for high molecular weight macromonomer (PSU-B-a-4) was lower than that of the corresponding the low molecular weight analogue (PSU-B-a-2). This behavior can be attributed to the dilution effect as higher molecular weight contains less number of benzoxazines for unit weight. Similar

behavior was observed with the other polymeric benzoxazines [51,53,223]. Interestingly, in both cases, the glass transition temperatures (T_g) were detected at higher temperature after the curing reaction due to the restricted mobility of PSU chains as presented in Figure 4.4 and Figure 4.5 by the second DSC runs. The network structures exhibited T_g temperatures at around 170 ^{o}C.

In order to gain more insight on the effect of molecular weight, further thermal analysis was conducted by eliminating weight contribution to heat flow. In Figure 4.6, DSC thermograms of benzoxazine end-capped polysulfone macromonomers with different molecular weights, obtained by dividing energy units (Watts) to sample weights (g), were overlaid. As can be seen, the maximum heat flows become lower as the molecular weight increases. The maximum curing temperatures of macromonomers are close to each other since benzoxazine moieties are surrounded by the same chemical environment in all cases.

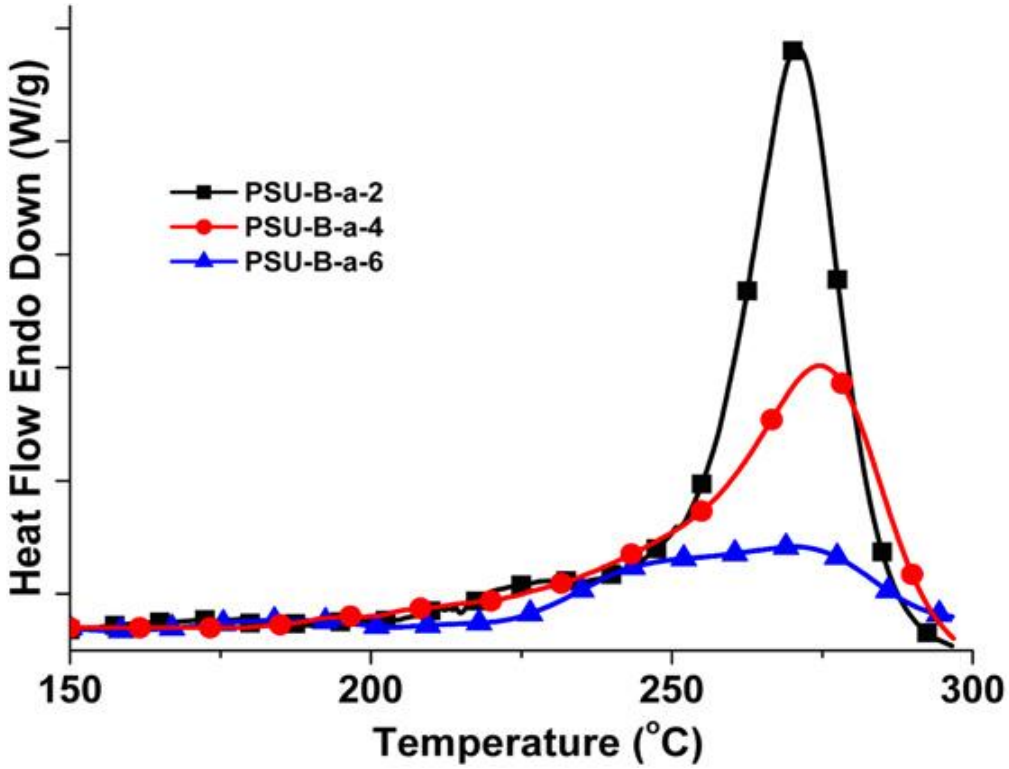


Figure 4.6 : DSC profiles of PSU-B-a with different molecular weights.

The effect of P-a content on thermal properties of PSU-B-a was also studied. DSC thermograms of the benzoxazine end-capped PSU macromonomer, mono-functional aniline derived benzoxazine monomer P-a and PSU-B-a/P-a blends with two different weight percentages (10% and 20%) are shown in Figure 4.7. As can be

seen, PSU-B-a shows higher exotherm temperature since the concentration of the oxazine ring is low due to the dilution of the reactive ring by the non-reactive sulfone chain. Thus, by having more concentration of the telechelic molecules, the exotherm temperature increases. As the P-a content increases the concentration of the telechelic molecules decreases and therefore the ring opening exothermic peak shifts toward a lower temperature.

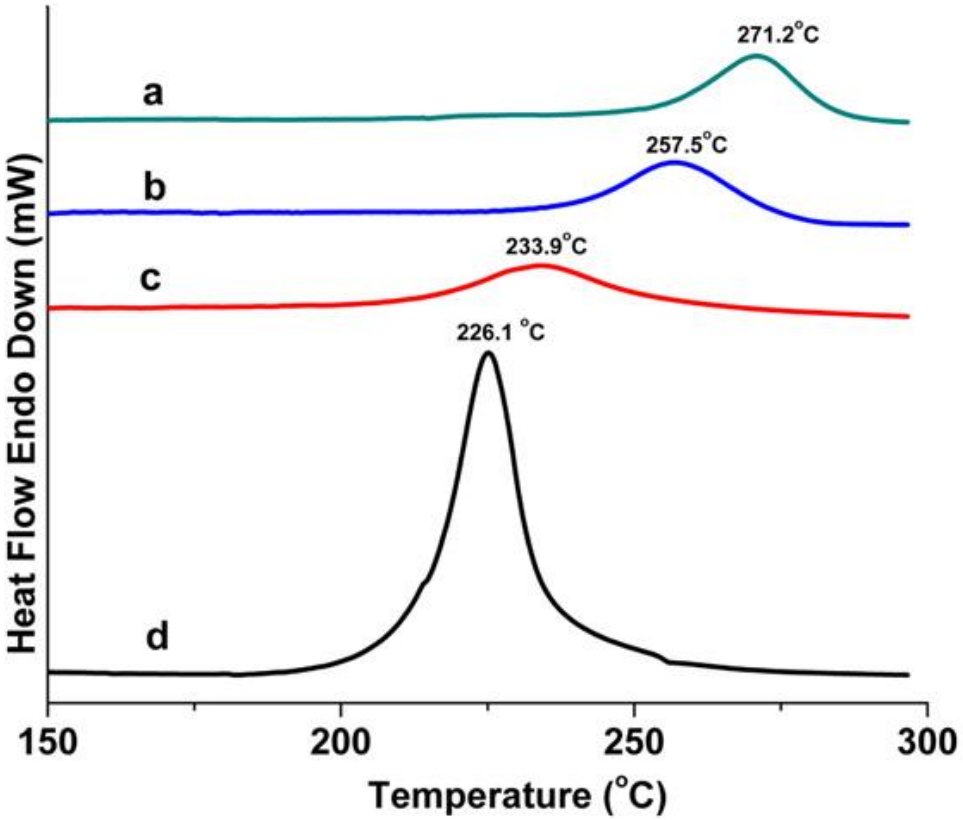


Figure 4.7 : DSC profiles of PSU-B-a/P-a blends at various compositions; 100% PSU-B-a-2 (a); 90 wt % PSU-B-a-2 / 10 wt % P-a (b); 80 wt % PSU-B-a-2, 20 wt % P-a (c) and 100% P-a (d).

Temperature related progress of ring-opening polymerization of the PSU-B-a was monitored by DSC. Figure 4.8 shows DSC thermogram of PSU-B-a-2 after each pretreatment. The amount of exotherm decreased with the increase of heat treatment temperature. The exotherm completely disappeared after 200 ^{o}C heat treatment for 2h, indicating that ring-opening of oxazine was completed.

4.1.3 Thermogravimetric analysis

Thermal stability of the thermally cured PSU-B-a was investigated by TGA and compared with those of the precursor PSU-OH and the mono-functional aniline

derived benzoxazine P-a. The TGA profiles presented in Figure 4.9 indicate that PSU-B-a showed much higher thermal stability than the precursor PSU-OH.

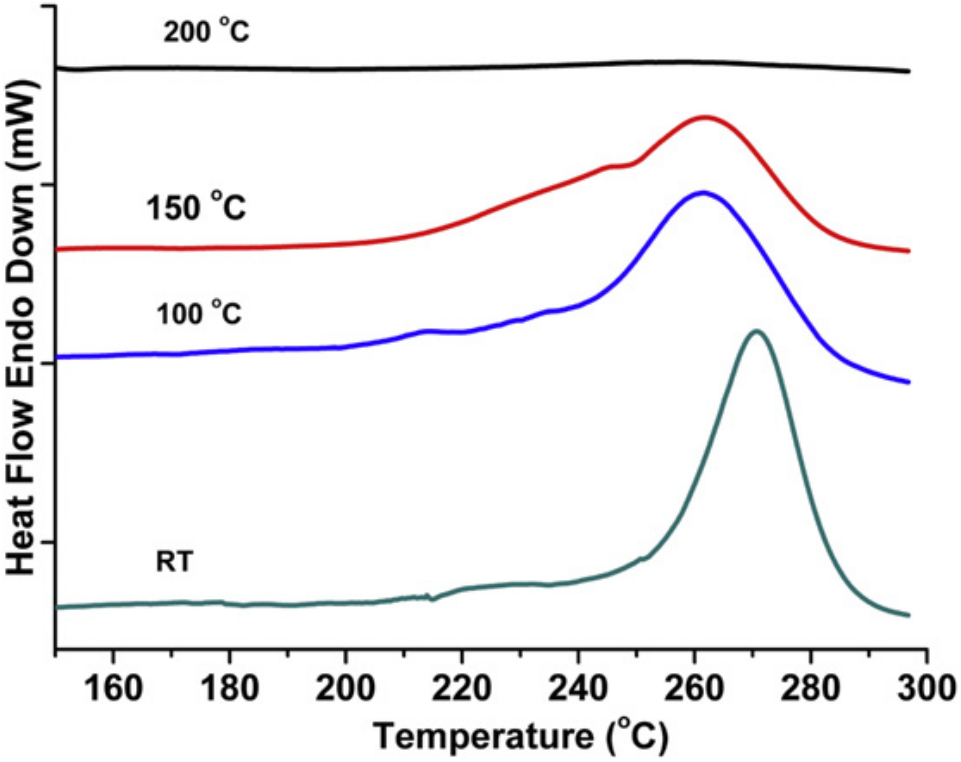


Figure 4.8 : DSC thermogram of PSU-B-a-2 after thermal treatment at different temperatures for 2 h.

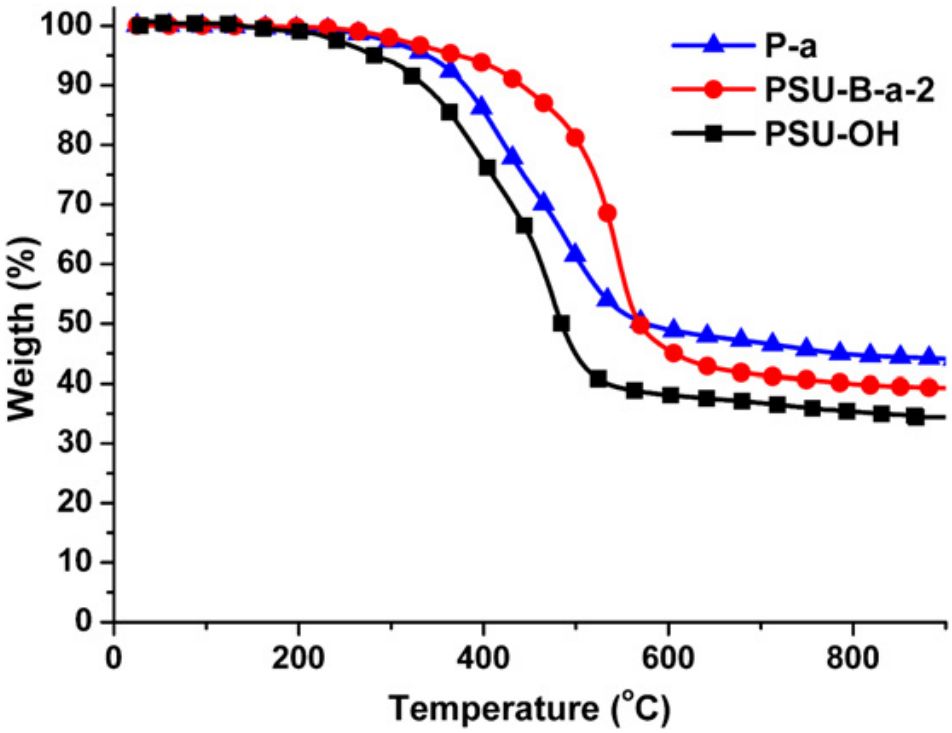


Figure 4.9 : TGA thermograms of phenol-ended telechelic (PSU-OH), benzoxazine endcapped macromonomer (PSU-B-a) and P-a cured at 200 °C for 4 h.

Main degradation occurred at 440 ^{o}C which is well above that of polybenzoxazine (PP-a). It should be pointed out that he crosslinked structure changes when polysulfone and benzoxazine groups are combined in the network. The additional hydrogen bonding arising from polysulfone segment may contribute to the increased thermal stability. Similar thermal behavior was also observed with thermosets obtained from poly(ether ketone) based benzoxazine macromonomers [51]. The char yield of the thermally cured PSU-B-a (39%) at 900 ^{o}C is high in comparison to PSU-OH (34%) due to the benzoxazine end groups and close to that of polybenzoxazines such as PP-a (44%).

4.1.4 Tensile properties

Representative stress-strain curves of P-a, PSU-B-a-2 / 10 wt % P-a and PSU-B-a-4 / 10 wt % P-a are shown in Figure 4.10 and tensile properties are summarized in Table 4.2. The modulus is obtained from the initial slope of the stress-strain curves. As can be seen in Figure 4.9, the highest modulus and the lowest elongation were observed in P-a polymer.

The tensile modulus decreased in PSU-B-a / P-a films with increasing chain length. This is expected since the molecular weight of polymer is related to the probability of chain end reaction. The shorter chains favor the interaction of benzoxazine end groups to form the network structure which stiffened the macromolecular chain. However, the elongation at break increased with increase in the chain length.

Table 4.2 : Tensile properties of P-a, PSU-B-a-2 / 10 wt% P-a and PSU-B-a-4 / 10 wt% P-a films after curing

Sample	Toughness[a] (kPa)	Modulus (kPa)	Strength (kPa)	Elongation at break (%)
P-a	11	516	191	37
PSU-B-a-2/10 wt% P-a	69	237	315	139
PSU-B-a-4/10 wt% P-a	113	153	299	195

[a] Calculated from the area under the stress-strain curve.

The toughness of the polymers was calculated from the area under the stress-strain curves and the values are shown in Table 4.2. The highest toughness was observed with PSU-B-a-4 / 10 wt % P-a. As a result, PSU-B-a / P-a films exhibited enhanced toughness over the P-a polymer.

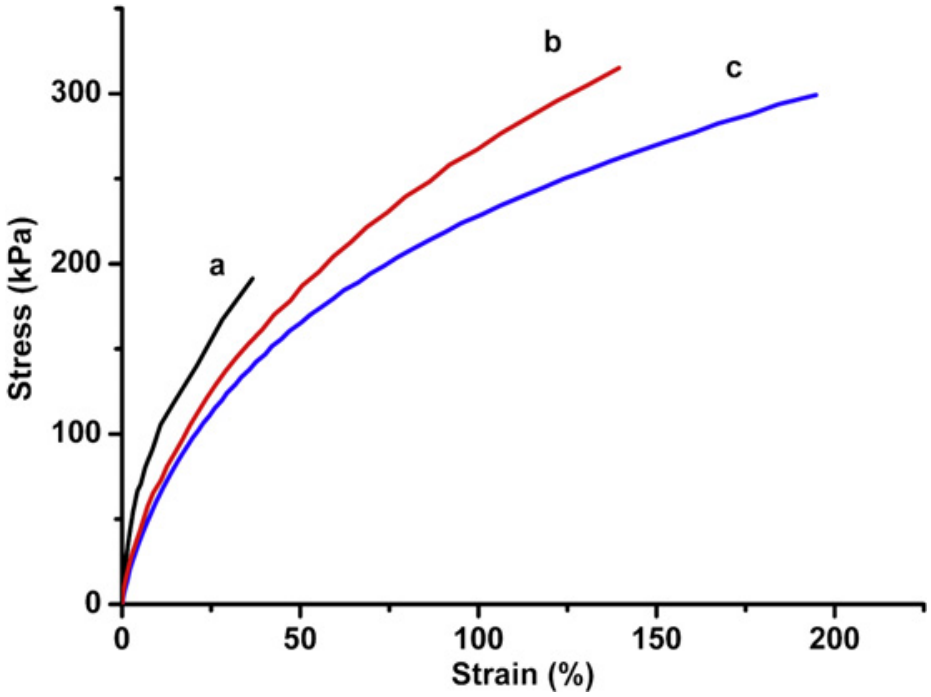


Figure 4.10 : Stress-strain curves of P-a (a), PSU-B-a-2 + wt 10 % P-a (b) and PSU-B-a-4 + wt 10 % P-a (c) cured at 200 ^{o}C for 4 h.

4.2 Synthesis and Characterization of Polysulfone-g-poly(2-alkyl-2-oxazoline)s

4.2.1 Synthesis of PSU macroinitiators

The synthesis of amphiphilic graft copolymers of PSU with poly(2-alkyl-2-oxazoline) (PAOx) graft arms was carried out in two steps (Figure 4.10). The first step involves synthesis of chloromethylated PSU (PSU–CH_2Cl) which is used as the macroinitiator of graft copolymerization. The evidence of successful chloromethylation of PSU was demonstrated by presence of the peak at δ 4.50 ppm in ^{1}H NMR spectrum (Figure 4.11). The proportion of chloromethylated repeating units on PSU chains (degree of chloromethylation) was determined by the integration values of ^{1}H NMR signals corresponding to peak at 4.50 (f) and the reference peak at 7.76 (e) belonging to meta protons on the benzene ring near to the sulfonyl group. The degree of chloromethylation is calculated 0.15.

4.2.2 Synthesis of graft copolymers

The second step includes grafting reaction of 2-methyl-2-oxazoline (MeOxa), 2-ethyl-2-oxazoline (EtOxa) and 2-propyl-2-oxazoline (PrOxa) initiated by the chloromethylated PSU by using grafting from method (Figure 4.11). Schematic representation of formation of graft copolymers is demonstrated in Figure 4.12.

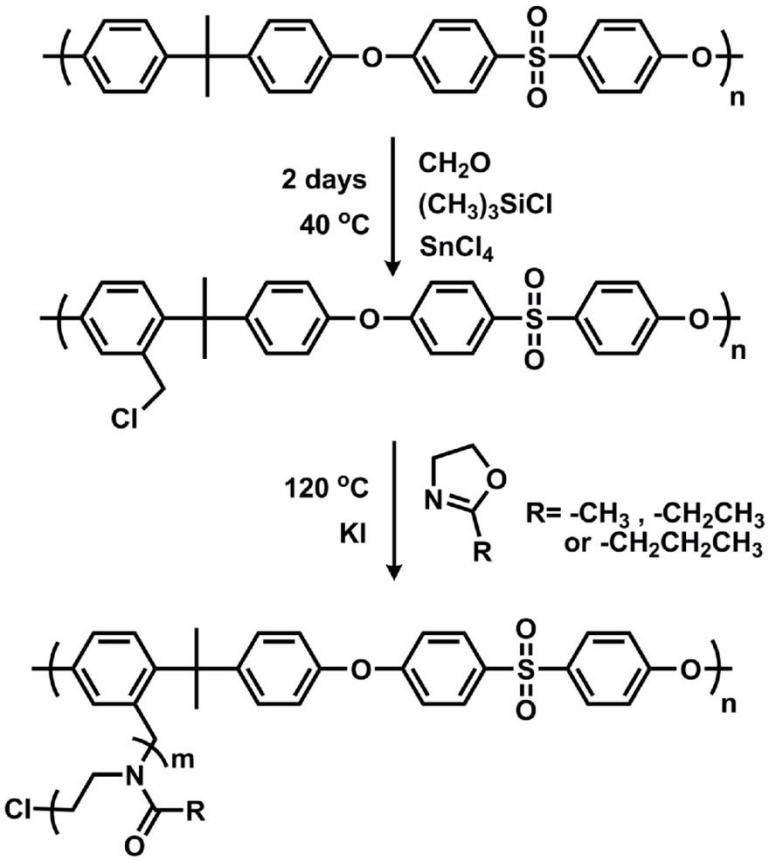


Figure 4.11 : Synthesis route of PSU-g-poly(2-alkyl-2-oxazoline).

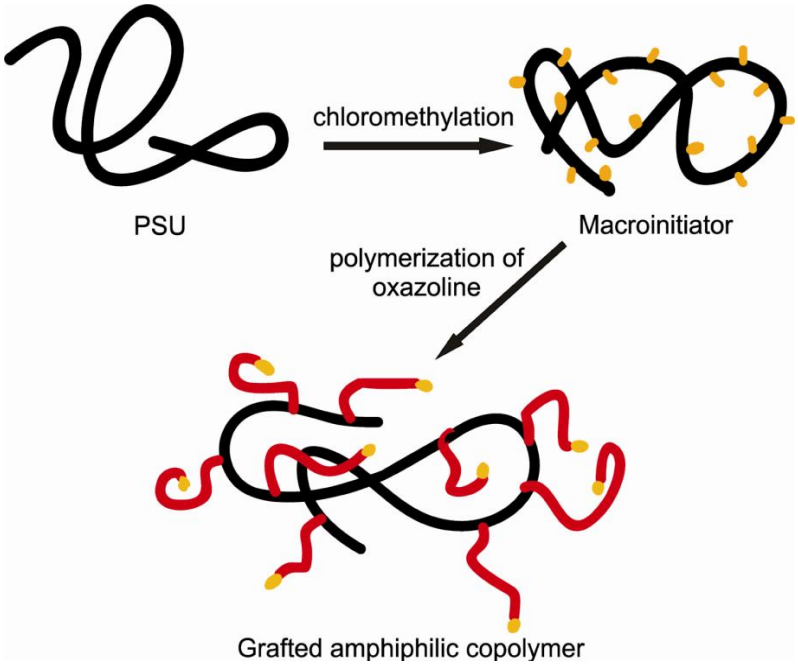


Figure 4. 12 : Formation of the graft copolymer.

The ring opening polymerization was carried out at 120°C in bulk and potassium iodide was used as activator. The macroinitiator was soluble in the oxazoline

monomers so that bulk polymerization was conducted. The macroinitiator and KI were carefully dried under vacuum to achieve anhydrous conditions for the reaction.

The graft copolymer products (G) were soluble in the polymerization medium so during the reaction, solutions remained homogeneous. Blank tests were performed for all the oxazoline monomers in the absence of the macroinitiator with same conditions. No graft copolymer formation was observed in all cases.

The ^{1}H NMR spectra of the graft copolymers (e.g. G4) undoubtedly confirms the characteristic signals of the backbone PSU and the signals of the polyoxazoline graft arms (Figure 4.13). Typically, signals of methylene protons on backbone of the grafted chains appear between 3.3–3.7 ppm for all the polyoxazolines. Furthermore, chemical shifts of alkyl substitutions of the oxazolines appear relatively up fields. Since the molar ratios of repeating units in graft arms to PSU repeating units are too high, the signals of the backbone of PSU are weaker (getting weaker from G3 to G6) but noticeably visible (Figure 4.14). The signal of connecting unit between the backbone and the graft arm is not recognizable because of its too low concentration compare to the signals of repeating units. In the 'H NMR spectra, the signal at 4.5 ppm of the benzylchloride protons of the macroinitiator disappeared in GP4 which may point out that almost all initiator sites did react.

Further confirmation of successful graft copolymerization is shown in Figure 4.15 in which the FT-IR spectrum of the graft copolymer (GP4) shows a band of the amide carbonyl groups (1630 cm') and bands of C–H bonds between 1370 and 1470 which do not exist in the spectrum of the macroinitiator.

GPC measurements for graft copolymers was not possible since the amphiphilic character of graft copolymers and their strong interactions with the column material provoke broad distribution traces and absurd values [224].

In the absence of potassium iodide, polymerization is started by benzylchloride functions and in the propagation step it proceeds by covalent mechanism since the nucleophilicity of the chloride anions larger than the oxazolines. [73,86,227], Addition of potassium iodide turns the benzyl chloride functional groups into benzyl iodide functions. Thus, the propagation step takes place by cationic ring opening mechanism which is faster than covalent one because iodide anion is comparatively weak nucleophile [66,226]. The polymerization of EtOxa or PrOxa was much faster

than of MeOxa because it might take place dominantly by cationic ring-opening mechanism but in contrast MeOxa polymerization might occur through covalent mechanism in spite of presence of KI. For this reason, yield of MeOxa polymerization was obtained less than 4% after 144 h whereas yield of both EtOxa and PrOxa polymerization reaches to 55% even after 24 h (Table 4.3).

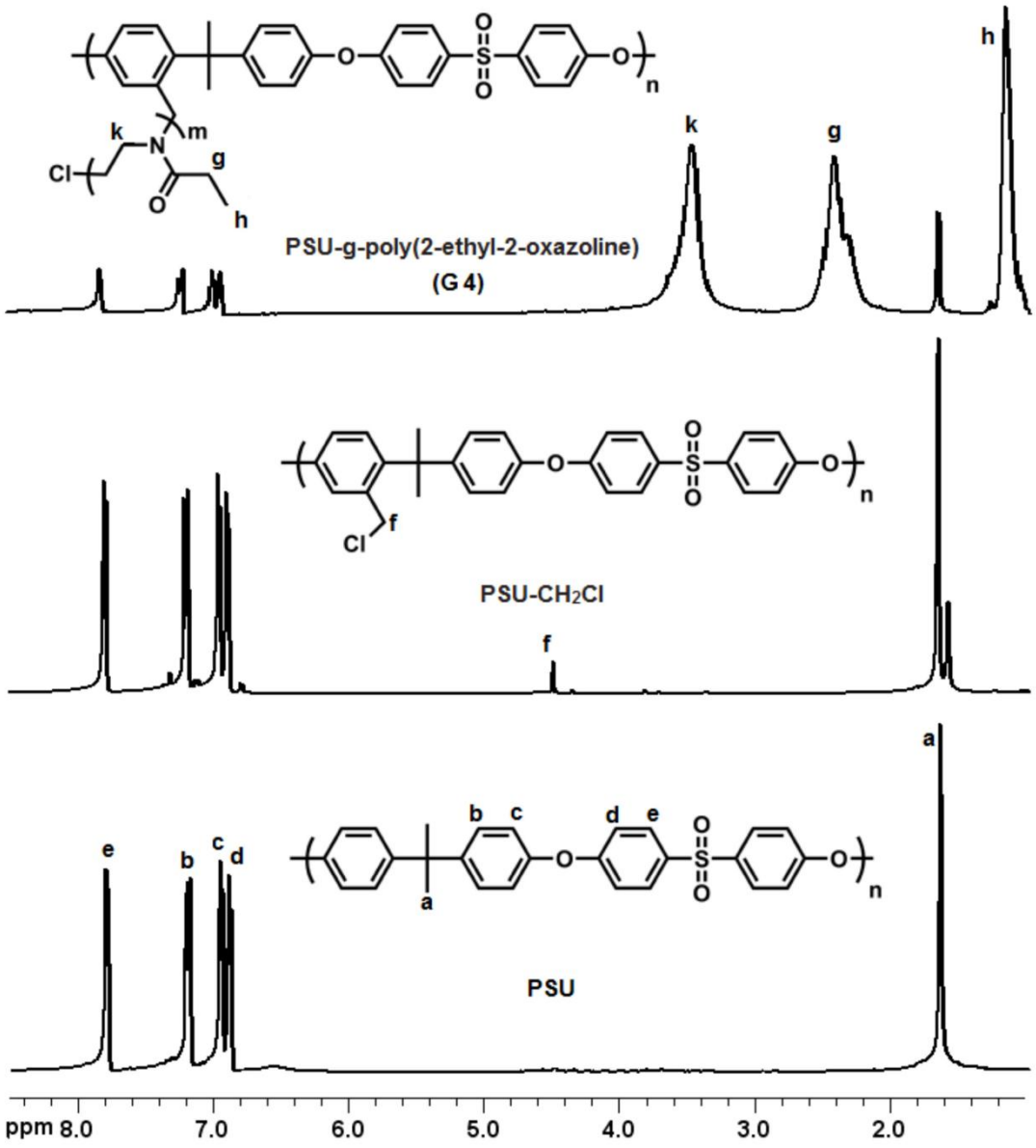


Figure 4.13 : ^{1}H NMR spectra of PSU, the macroinitiator PSU-CH_2Cl and PSU-g-poly(2-ethyl-2-oxazoline) (PSU-g-PEtOx).

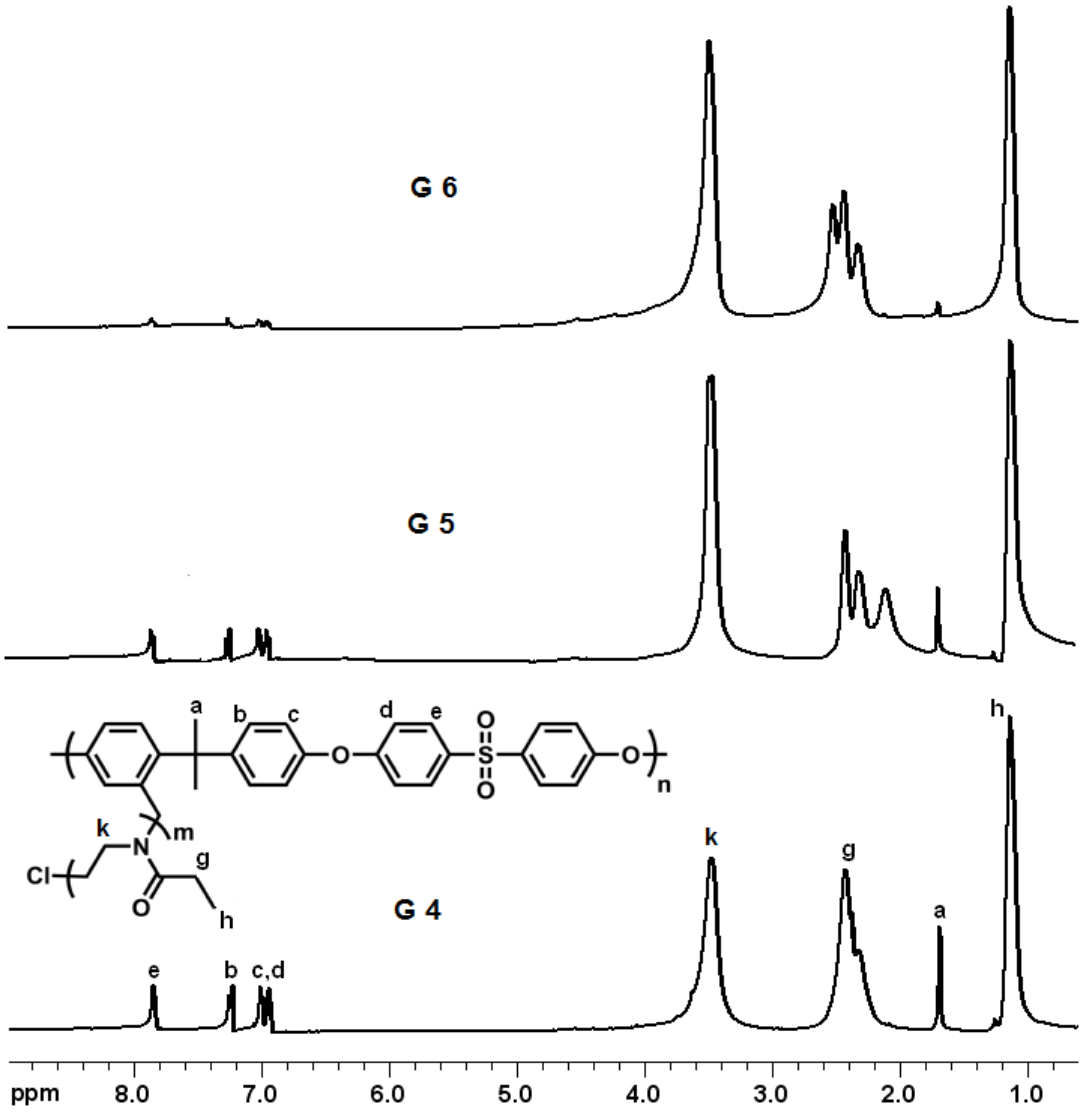


Figure 4.14 : ^{1}H NMR spectra of PSU-g-PEtOx copolymers.

Mole ratio of grafted polyoxazoline repeating units and macroinitiator repeating units was calculated from yield and alternatively from integration values of corresponding peaks in ^{1}H NMR spectra under the acceptation of 100% initiator efficiency of the benzylchloride functionalities. For this purpose, integration of meta protons signal (e) at 7.83 ppm and methylene signal of the polyoxazoline graft arm (k) at 3.5 ppm were utilized. Both results derived from the ^{1}H NMR and the yields are compatible and close to each other. The degrees of polymerization of the graft arms are obtained in the range from 80.4 to 616.2 for EtOxa and PrOxa and 25.8 to 62.8 for MeOxa. Therefore, the results agree with the linear time-conversion relation (the "living" character) of the polymerization of 2-alkyl-2-oxazolines.

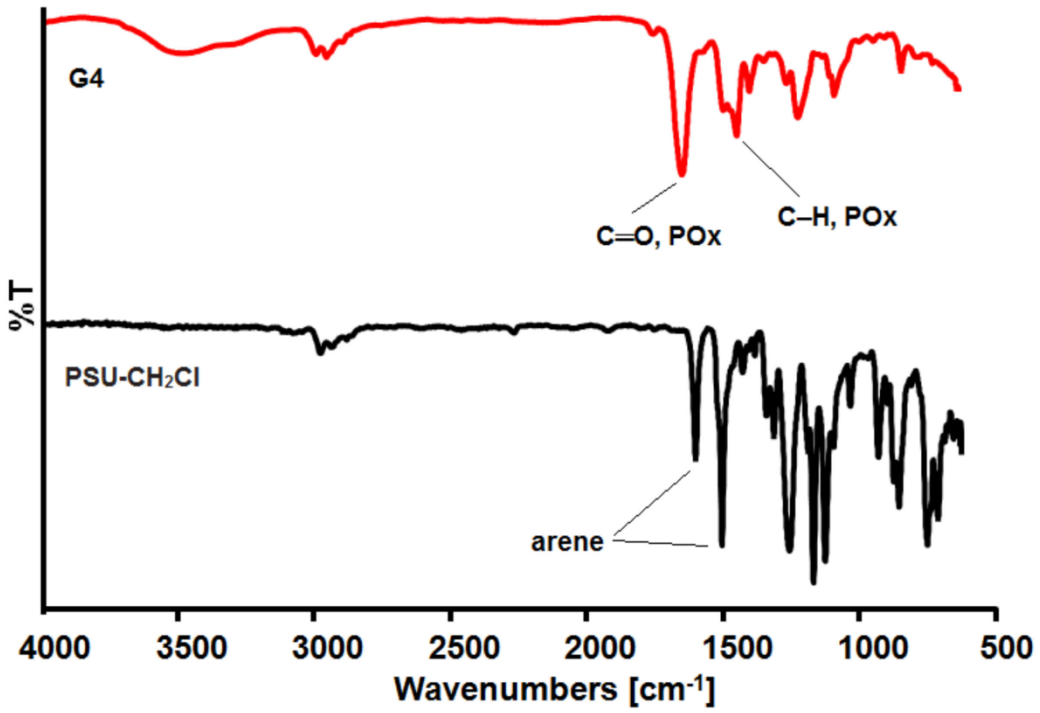


Figure 4.15 : ATR-FTIR spectra of PSU-CH_2Cl and PSU-g-poly(2-ethyl-2-oxazoline).

Table 4.3 : Synthesis of PSU-*g*-poly(2-alkyl-2-oxazoline)s by cationic ring opening polymerization in bulk at 120 °C in the presence of KI ($8x10^{-3}$ mol/L) using PSU-CH_2Cl (M_n=29000).

Code	Monomer	Reaction time (h)	Yield[a] (%)	[POx]/[PSU] (mol/mol)[b]		DPn[c]	T_g (°C)	M_n[d] (g/mol)
				from yield	NMR			
G1	MeOx	24	1.8	3.9	1.8	25.8	N/A	49300
G2	MeOx	144	3.6	7.8	7.6	62.6	N/A	70180
G3	EtOx	0.50	6.5	12.1	10.4	80.4	62.1	102660
G4	EtOx	0.83	11.2	20.9	15.3	138.5	50.6	156600
G5	EtOx	2	17.1	30.0	24.5	199.9	49.2	223300
G6	EtOx	24	52.7	92.4	68.1	616.2	42.7	536500
G7	PrOx	2	17.5	27.4	21.3	182.9	N/A	255200
G8	PrOx	24	55.1	86.4	72.4	576.0	N/A	649600

[a] Yield of the graft copolymerization.

[b] Molar ratio of 2-alkyl-2oxazoline repeating units in graft arms and sulfone repeating units in backbone.

[c] Number averaged degree of polymerization of poly(2-alkyl-2-oxazoline) side chains.

[d] Determined from yield.

DSC studies exhibited single T_g values for the graft copolymers of PSU-g-PEtOx. This T_g corresponds to glass transition of PEtOx and varied from 62.1 ^oC to 42.7 ^oC for G3 to G6, respectively. The bulk T_g of PEtOx is 40-45 ^oC and of PSU is 185 ^oC. The increase in T_g of graft copolymers with decreasing molecular weight of side chains is due to decreased mobility of PEtOx side chains resulting from grafting to the rigid PSU backbone. As PEtOx side chain length increases, the effect of grafting on the mobility becomes less dominant and T_g value approaches to that of bulk PEtOx.

4.2.3 Physicochemical Characterization of graft copolymers

For further physicochemical investigations, we have spin coated thin films of PSU-g-PAOx on silicon substrates and characterized the films by atomic force microscopy to understand the effect of alkyl side chains on the morphology of the graft copolymers. Neither of the graft copolymers was soluble in water at room temperature, but they formed initially homogenous dispersions indicating their amphiphilic nature. All graft copolymers dissolved in THF and formed homogeneous solutions. Figures from 4.16 to 4.22 shows the AFM height images of graft copolymers spin coated from 1 mg/ml solutions in THF. Film thicknesses were ~8-12 nm as measured by ellipsometry.

Films of PSU-g-PMeOx (Figure 4.16 and 4.17) did not cover the whole substrate surface and contained holes. The mesh-like morphology in Figure 4.16 (G1, PMeOX/PSU mol ratio = 1.8) improved significantly with increasing mole fraction of PMeOx resulting in less and smaller holes in Figure 4.17 (G2, PMeOX/PSU mol ratio = 7.6). Among the 8 graft copolymers, the ones containing PMeOx side chains (G1, G2) had the smallest POx/PSU mole ratio and the largest volume fraction of PSU. The observed mesh-like morphology can be attributed to the less solubility of PSU in THF.

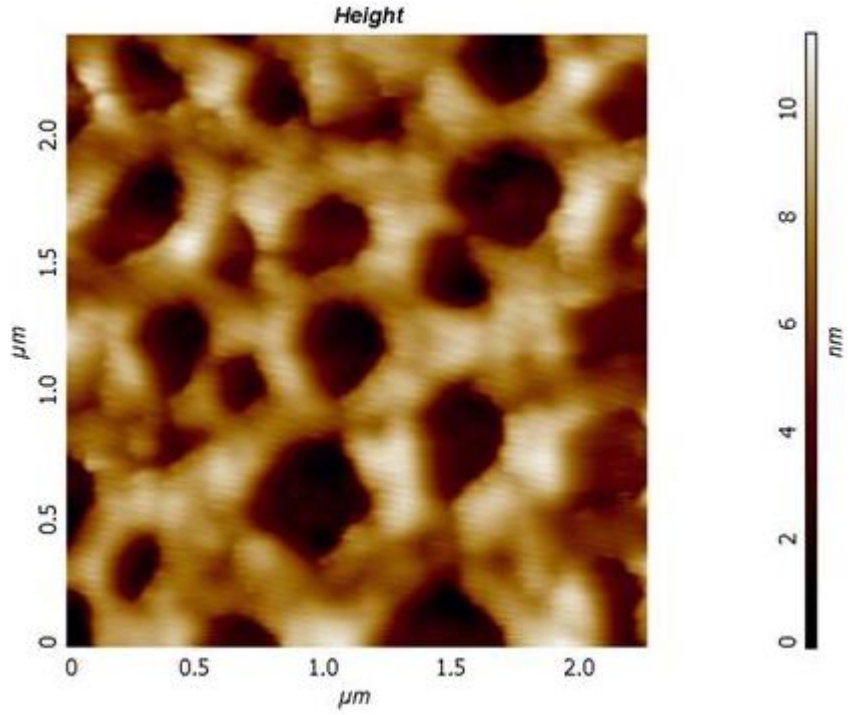


Figure 4.16 : AFM height images of G1.

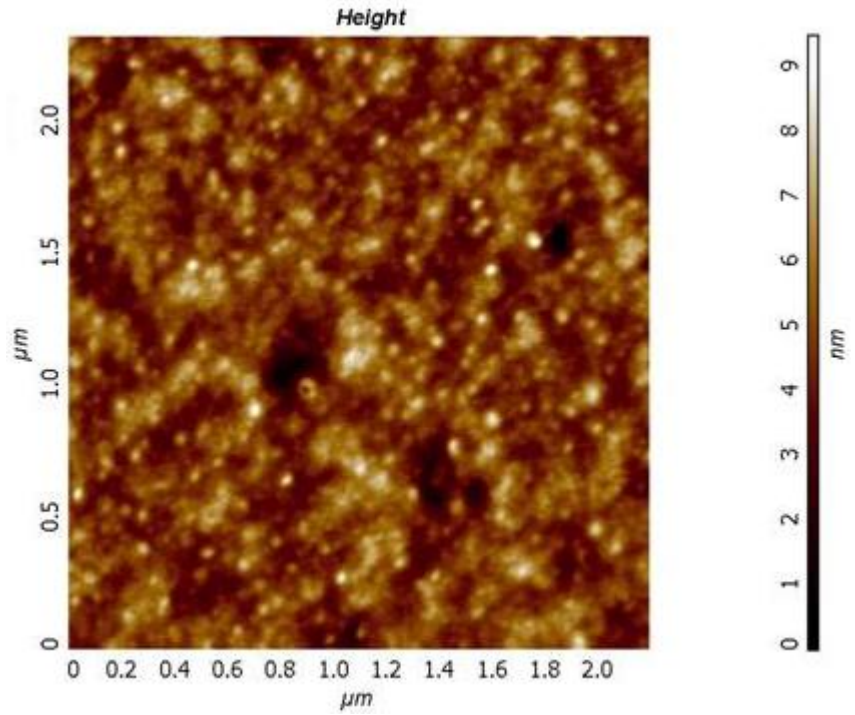


Figure 4.17 : AFM height images of G2.

Graft copolymers consisting of PEtOx and PPrOx (G3-G8) side chains all formed uniform films with significantly smaller surface roughness compared to PSU-g-PMeOx films. Figure 4.18, 4.19 and 4.20 show the morphology of PSU-g-PEtOx thin films having PEtOX/PSU mol ratio of 10.4 (G3), 24.5 (G5) and 68.1 (G6),

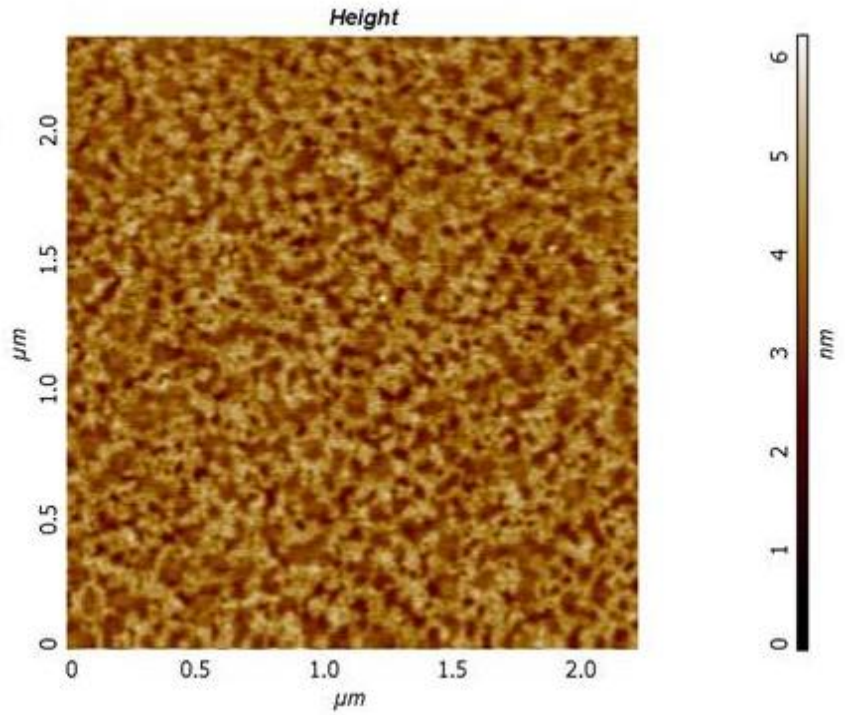


Figure 4.18 : AFM height images of G3.

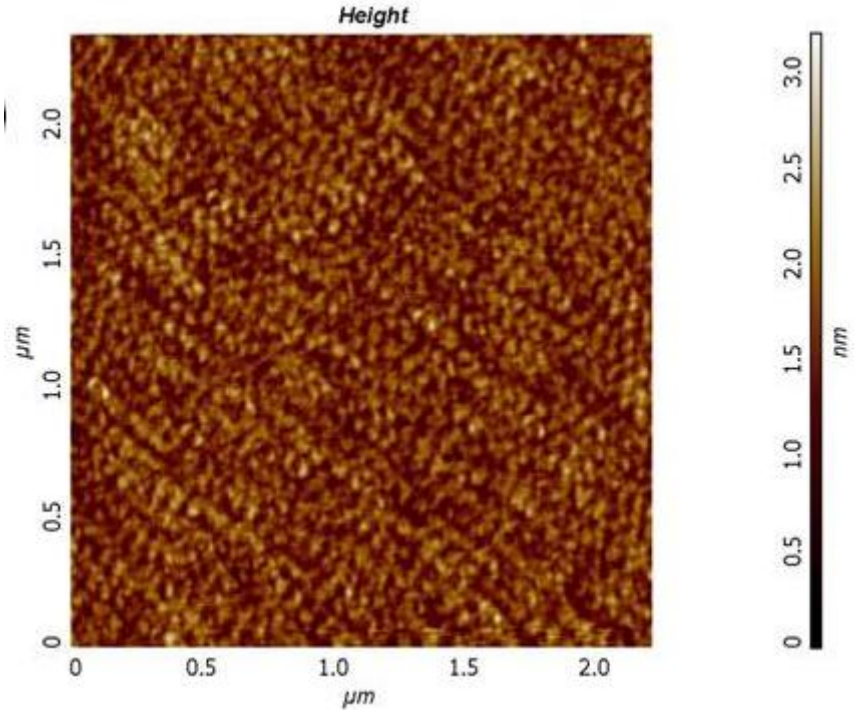


Figure 4.19 : AFM height images of G5.

respectively. Figure 4.18 clearly shows a multilayered film. The incomplete top layer has an average thickness of ~1.5 nm. The underlying layer is nearly complete with some holes having depth of ~1.5 nm. A layer thickness of 1.5 nm is consistent with

the degree of polymerization of the PEtOx side chains and this layered morphology shows the amphiphilic nature of the graft copolymers.

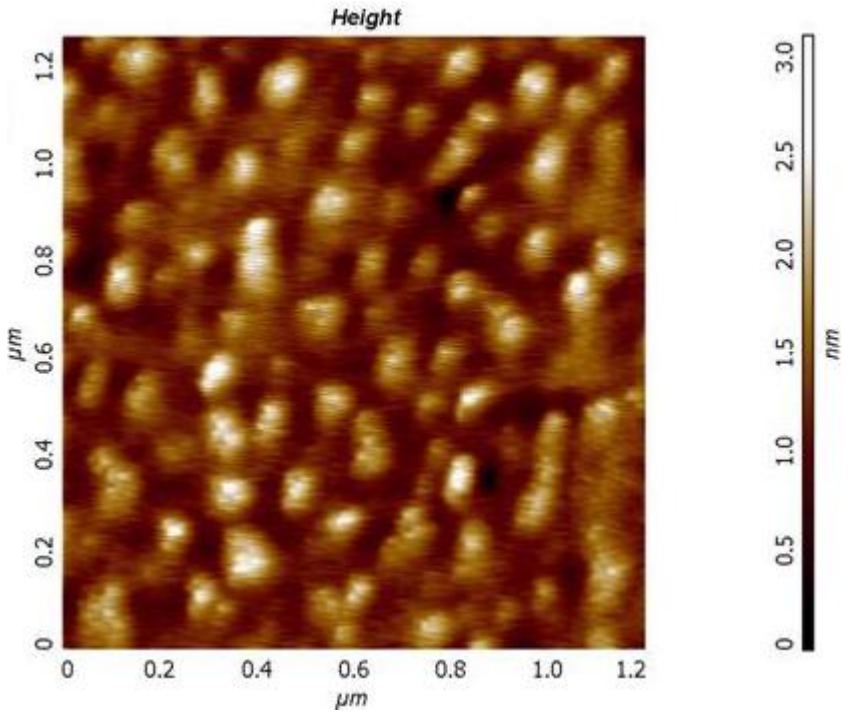


Figure 4.20 : AFM height images of G6.

Although the molecules are still amphiphilic at higher mole fractions of PEtOx, the volume fraction of PSU goes down to ~0.06 at PEtOX/PSU mol ratio of 68.1. The larger volume fraction of PEtOx dominates and the top surface of the films becomes smoother. In the case of PPrOx side chains (G7, G8), the volume fraction of PSU was also less than 0.15 and the similar smooth surfaces were observed in Figure 4.21 and 4.22.

G5 and G6 samples have been chosen for further physicochemical characterization to investigate the effect of PEtOx side chains on the morphology and the surface hydrophobicity of the graft polymers. Neither G5 nor G6 was soluble in water at room temperature, but they formed initially homogenous dispersions. The aggregate size as measured by DLS was ~0.85 μm for G6 and ~1.00 μm for G5. The higher EtOx/sulfone mole ratio for G6 (0.681) compared to that of G5 (0.245) caused smaller aggregates and more stable dispersion in water.

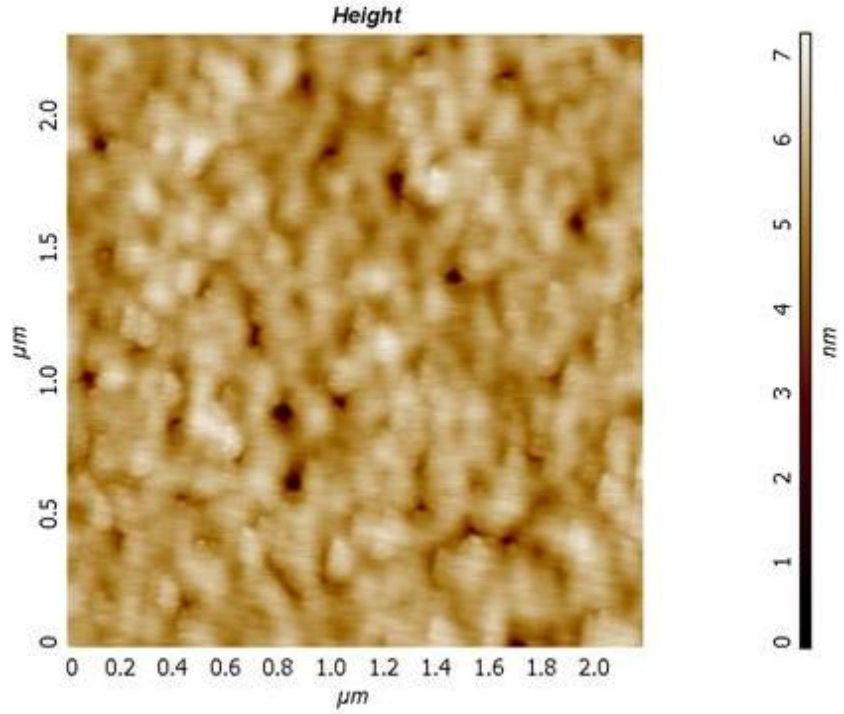


Figure 4.21 : AFM height images of G7.

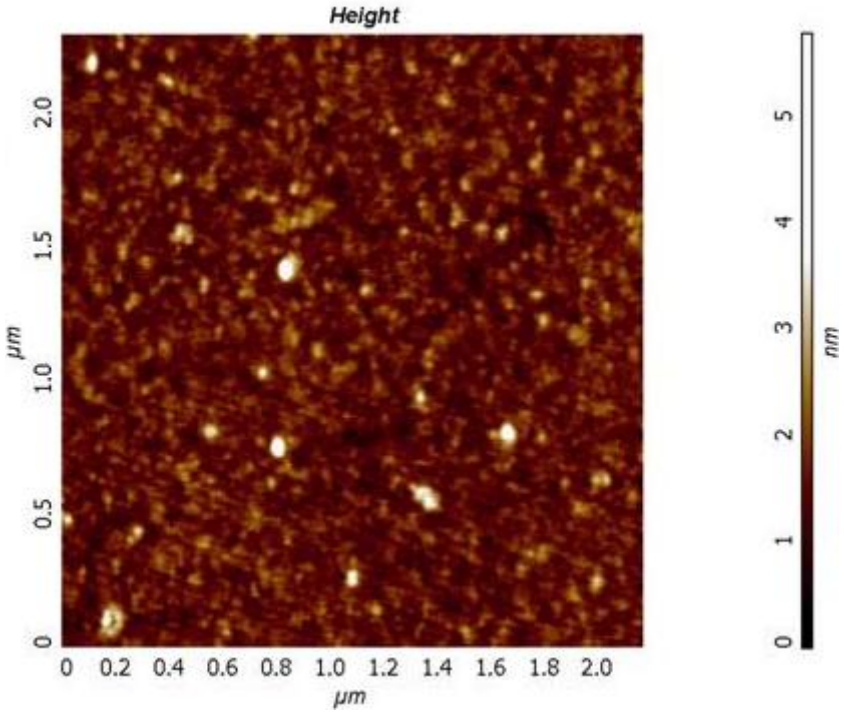


Figure 4.22 : AFM height images of G8.

Both polymers dissolved in $CHCl_3$. 100 nm thick films were spin coated on silicon oxide substrates from solutions in $CHCl_3$. The films were stable upon annealing above T_g of PEtOx at 80 ^oC for 3 hours. Water contact angle (CA) measurements were done on the films as a function of time using 4 µL water drops (Figure 4.23).

On G6 films, a stable CA of ~7^{o} was reached on both dried films and films annealed at 80 ^{o}C. Such low CA indicates that the top surface of the films predominantly contain the grafted hydrophilic PEtOx side chains. Since PEtOx is water soluble at room temperature, at such high PEtOx volume fraction, it is also possible that CA of 7^{o} is due to the penetration of water drop into the PEtOX regions. This possibility has further been investigated by temperature dependent CA measurements and discussed below.

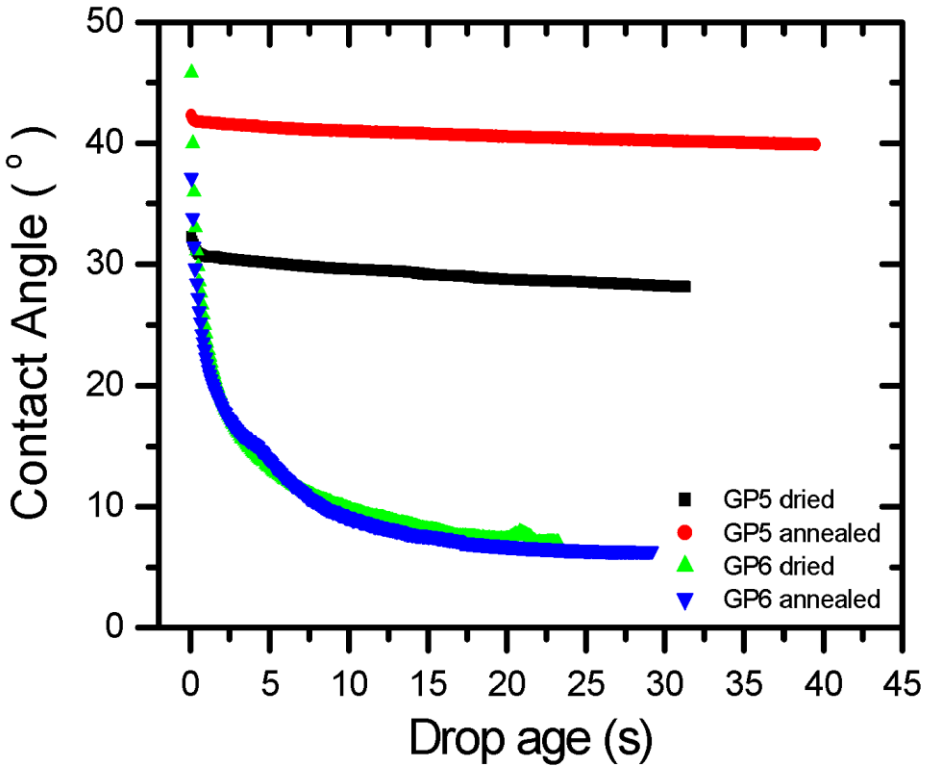


Figure 4.23 : Water contact angle as a function of time on spin coated G5 and G6 films.

The stable water CA on dried GP5 films was 30^{o}. A larger water CA compared to that on G6 films was consistent with smaller EtOx/sulfone mole ratio of 0.245 in the case of G5. When the films were annealed above T_g of PEtOx at 80 ^{o}C, the stable water CA increased to 40^{o}. This increase might either be due to PEtOX molecules to segregate away from the top surface into the film (increasing surface fraction of PSU on top) or due to increased hydrophobicity of PEtOx molecules after annealing.

Water CA measurements were done as a function of temperature (Figure 4.24) to understand the effect of temperature on the surface hydrophobicity. On G5 films, water CA increased gradually with temperature from 10^{o} at 10 ^{o}C to 33^{o} at 80 ^{o}C.

This gradual increase, even below the T_g of PEtOx, indicates that the surface hydrophobicity increases due to increase in the hydrophobicity of PEtOx rather than the change in the surface composition. On G6 films, the water CA increased from 7^o to 10^o up to 60 ^{o}C and the increase was steeper above 60 ^{o}C. We interpret that the kink at 60 ^{o}C corresponds to the cloud point temperature of aqueous PEtOx solutions at which PEtOx turns insoluble. A rather slow increase between 10 ^{o}C and 60 ^{o}C also supports that the water drops penetrate into PEtOx regions in G6 films.

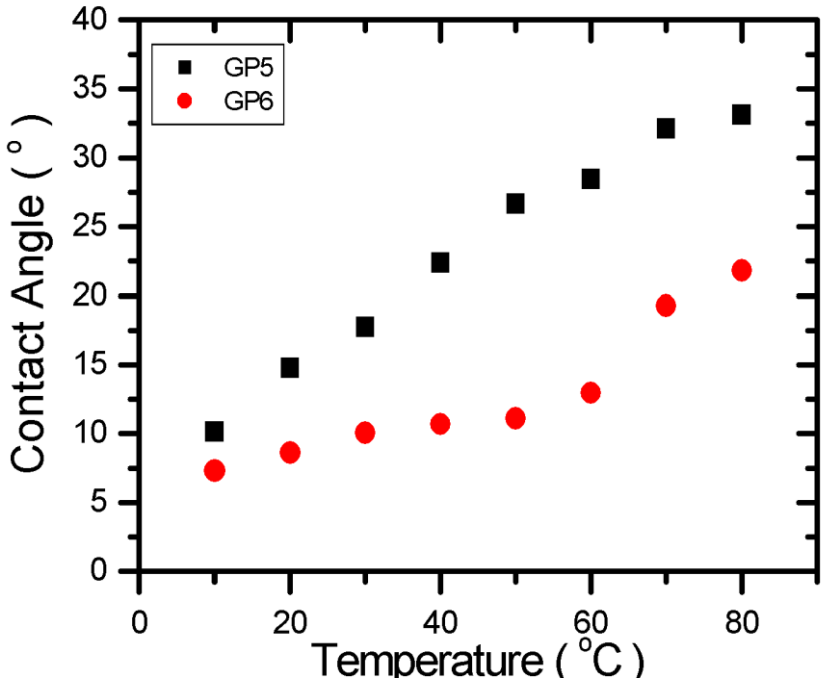


Figure 4.24 : Water contact angle as a function of temperature on spin coated G5 and G6 films.

The observation of larger water CAs on G5 than on G6 is consistent with EtOx/sulfone mole ratio as measured by ^{1}H NMR. Surface hydrophobicity investigations also show that both G5 and G6 surfaces are thermoresponsive in that the water CA changes with temperature. But, only on G6 surface at EtOx/sulfone mole ratio of 0.681, it was possible to see the critical temperature where the surface switches from being hydrophilic to hydrophobic.

The surface morphology of spin coated G5 and G6 films were annealed at 80 ^{o}C for 3 hours and investigated by AFM (Figure 4.25 to 4.28). 100 nm thick films of both G5 and G6 covered the underlying silicon oxide substrate uniformly. On both film surfaces, circular regions having sizes ~30-50 nm and heights ~2 nm were sporadically observed. The surface density of these regions was much larger for G5

than for G6. We attribute these regions to aggregated PSU backbones of the graft polymers. Due to the larger volume fraction of EtOx in G6, the number of these regions is much less on the G6 surface.

To be able to observe detailed information about the arrangement of PSU backbone and PEtOx side chains with respect to each other, we have investigated ~5nm thick films which did not cover the underlying substrates uniformly. Figure 4.26 shows the AFM height image of ~5 nm thick G5 film after annealing. Three different levels are clearly seen around the regions where the substrate was not covered: the substrate, a ~2 nm thick smooth film on the substrate and a ~5 nm thick film on top. We interpret this as ~2 nm thick PSU backbones on in touch with the underlying substrate and the grafted PEtOx side chains forming ~5 nm thick top layer. The ~2 nm thickness of PSU in Figure 4.26 is consistent with the thickness of circular regions observed in thicker films of Figure 4.25. The AFM height image of ~5 nm thick G6 film showed isolated island having a thickness of ~5-6 nm. We attribute these islands to PEtOx side chains. Due to the small volume fraction of PSU in G6, PSU regions were not clearly observed. PSU might be in touch with the underlying substrate as in the case of G5. There are also indications of PSU regions at the perimeters of these islands.

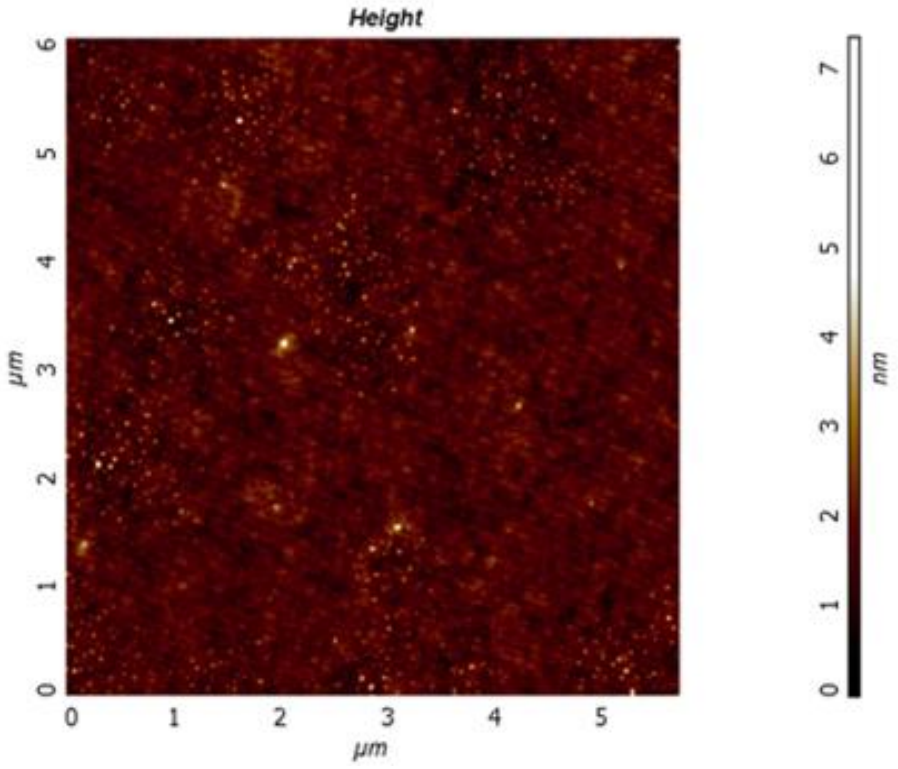


Figure 4.25 : AFM height images of spin coated 100 nm thick G5 film after annealing at 80 ^{o}C for 3 hours.

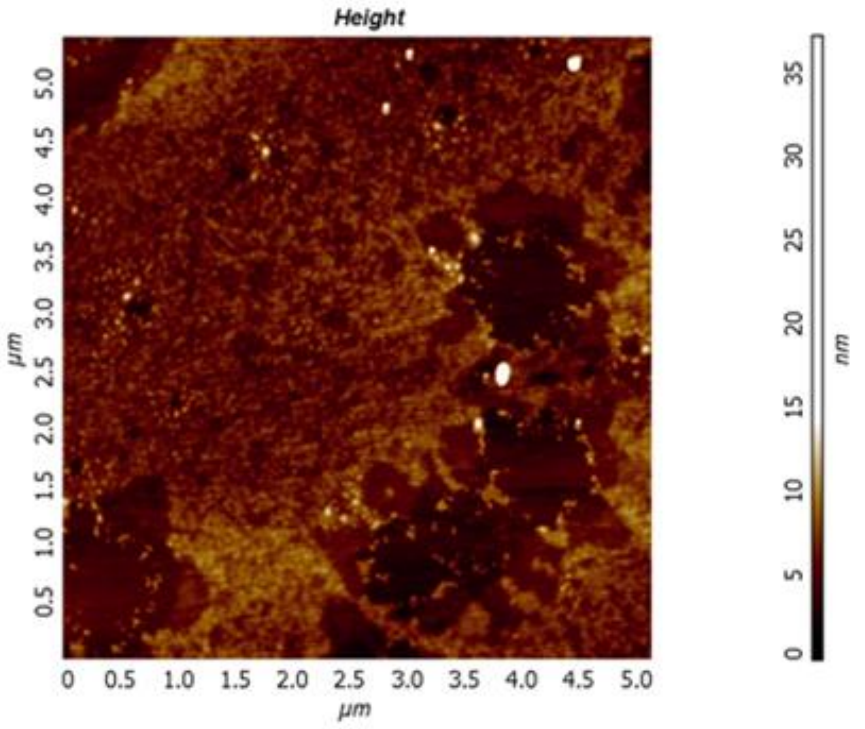


Figure 4.26 : AFM height image of spin coated ~5 nm thick G5 film after annealing at 80 ^{o}C for 3 hours.

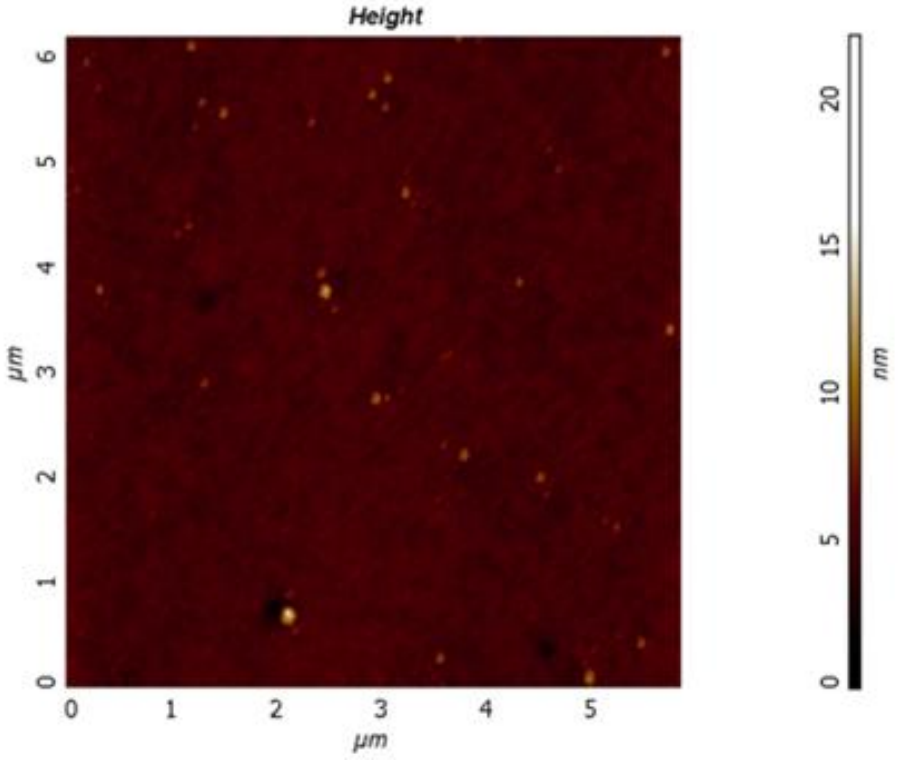


Figure 4.27 : AFM height image of spin coated 100 nm thick G6 film after annealing at 80 ^{o}C for 3 hours.

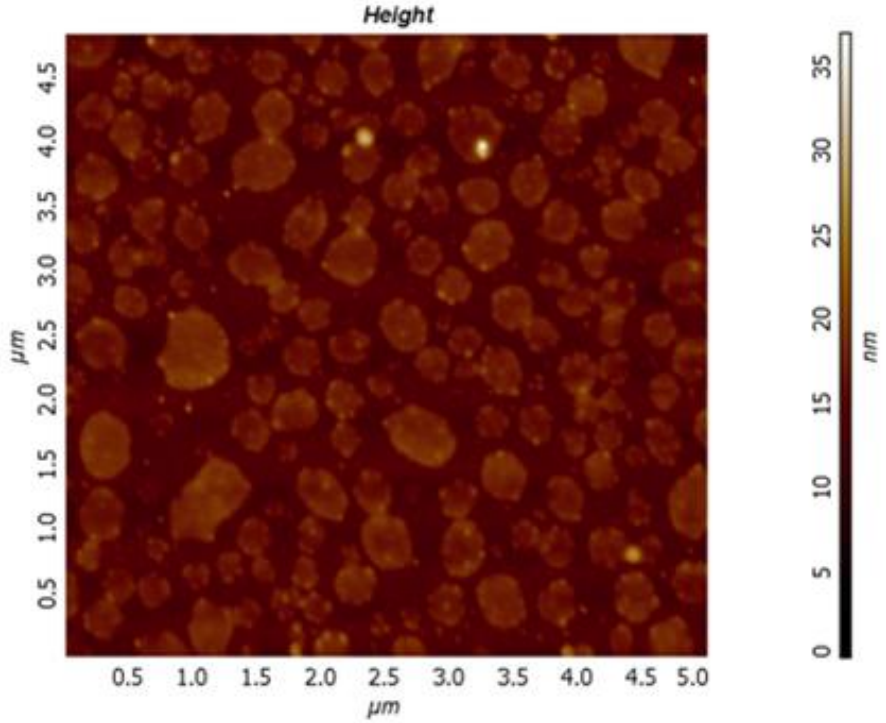


Figure 4.28 : AFM height images of spin coated ~5 nm thick G6 film after annealing at 80 ^{o}C for 3 hours.

5. CONCLUSIONS AND RECOMMENDATIONS

In the first part of this thesis, a new class of thermally crosslinkable oligomers (macromonomers) has been successfully synthesized. These oligomers consists of polysulfone structure as backbone with benzoxazine functional groups connected to both ends. The chemical structures of the intermediates and macromonomers were characterized by ^{1}H NMR, FT-IR and GPC. The free standing films of the reactive macromonomers can be further crosslinked by thermal activation to produce the tough films with good thermal stability. The effect of the molecular weight of PSU oligomer on the curing behavior, thermal and tensile properties was investigated. Hereby, combination of PSU with benzoxazine resins via end group functionalization results a synergic effect that improve thermal and mechanical properties of the polymeric system. Accordingly, PSU as an engineering thermoplastics can be a good candidate to overcome the problems associated with the brittleness and stiffness of benzoxazine based thermosets. Furthermore, benzoxazine moieties improve the thermal stability of PSU by enhancement in the degradation temperature and the char yield. Eventually, the thermal and mechanical stability of the cured films could further extend the use of PSU based membranes in application under severe conditions.

In the second part, amphipihilic graft copolymers of PSUs with well-defined POx chains as lateral substituents, were synthesized by combination of chemical modification of PSU backbone and cationic ring opening polymerization. Combined with the outstanding properties of PSU, it is frequently used as biomaterials since it can endure all sterilization techniques (steam, ethylene oxide, gamma radiation). Membrane technologies and biomedical applications such as hemodialysis, water purification, gas separation, cell culture, drug delivery, bioartificials and fuel cells require easy manufacturing processes allowing reproducible properties and controllable pore size. However, the hydrophobic nature of PSU restricts its usage as biomaterials in the filtration of protein containing solutions and blood containing applications. Modification of PSU with hydrophilic groups or segments overcome

these problems associated with the hydrophobicity. Among a variety of modification techniques for imparting amphiphlic character to PSU reactive functionalization followed by polymerization through this functional groups was utilized. Typically, chloromethylation were used to introduce initiating or reactive sites for blocking and grafting of hydrophilic monomers or oligomers, respectively. The structure, morphology and surface properties of such complexed macromolecules have been fully characterized. Because of the amphihilic nature of copolymers, they exhibit layered morphology in thin films when the PSU volume fraction is ~0.15 and above. The temperature dependent surface hydrophobicity of PEtOx films was also observed by water CA measurements. Consequently, the combination of the properties of both backbone PSU and side chain POx imply that these graft copolymers are promising biomaterials and may find many applications in various areas.

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